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POHC ANALYSIS METHODS FOR HAZARDOUS WASTE INCINERATION

Volume 1, Part 2

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16. ABSTRACT The report gives preliminary data on methodology for candidate principal organic hazardous constituents (POHCs) that represent a variety of compound types, including alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acids, aliphatic and aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics. This work (and that under Contract 68-02-2685, Task 111) involved the evaluation of generalized GC/FID, GC/MS, and HPLC/UV methods for determining approximately 170 compounds from the approximately 400 compounds in Appendix VIII, Part 261, 40 CFR. However, the survey-analysis portion of waste characterization often targets specific compounds for determination in incinerator effluent that are not amenable to previously developed methods. Therefore, current research involves the development of specific GC/FID, GC/MS, and HPLC/UV methods for the determination of several of these compounds. The EPA has proposed regulations for owners and operators of facilities that treat hazardous wastes by incineration to ensure that these incinerators will be operated in an environmentally responsible manner. The primary criterion upon which the operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator (= or > 99.99%).

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Pollution	Mass Spectroscopy	Pollution Control	13B
Incinerators	Ultraviolet Spectroscopy	Stationary Sources	
Analyzing		Principal Organic Hazardous Constituents	14B
Organic Compounds			07C
Hazardous Materials		Liquid Chromatography	13L
Toxicity		Destruction and Removal Efficiency (DRE)	06T
Gas Chromatography			07D

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

This report has been prepared by Southern Research Institute as part of ongoing studies in support of regulatory programs of Environmental Protection Agency's (EPA's) Air and Energy Engineering Research Laboratory, Research Triangle Park, North Carolina. This report contains criteria for the analysis methods for determination of principal organic hazardous constituents (POHCs) from the combustion of hazardous waste. The data in this report are intended as a reference to be used by laboratories that are monitoring the hazardous-waste streams of incineration facilities. Because of subtle differences among laboratories and analytical instrumentation, analysts who participate in similar studies should generate data that will establish their own criteria for the analysis of POHCs.

ABSTRACT

As part of the Resource Conservation and Recovery Act of 1976, the U.S. Environmental Protection Agency has proposed regulations for owners and operators of facilities that treat hazardous wastes by incineration to ensure that these incinerators will be operated in an environmentally responsible manner. The primary criterion upon which the operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. The DRE value, defined in terms of waste-input and stack-output levels of designated principal organic hazardous constituents (POHCs), must be equal to or greater than 99.99%.

In support of the DRE requirement, we evaluated and, when necessary, modified generalized GC/FID, GC/MS, and HPLC/UV analysis methods for the determination of approximately 100 candidate POHCs. These candidate POHCs represent a variety of compound types, including alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acids, aliphatic and aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics.

The developed generalized GC/MS and HPLC/UV methods are suitable for inclusion in the POHC Method Manual, Sampling and Analysis Methods for Hazardous Waste Combustion (EPA-600/8-84-002). The methods were applied to the determination of candidate organic compounds over concentration ranges of interest and demonstrated acceptable precision in the determination of most of the compounds.

We then applied these methods in a preliminary study to determine the recovery of selected POHCs from Amberlite XAD-2 sorbent. The sorbent was spiked with milligram quantities of 25 POHCs, internal standards, and surrogate standards, challenged in a simulated sampling system, and extracted with methylene chloride. The extracts were analyzed by the generalized methods. We have demonstrated that a series of POHCs can be successfully recovered from XAD-2 sorbent tubes.

Finally, we applied the GC/MS survey methods to the analysis of incinerator-effluent sample extracts. POHCs and other organic compounds were tentatively identified and quantified in the samples.

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ABBREVIATIONS AND SYMBOLS

amu	Atomic Mass Unit
Appendix VIII	Hazardous Constituents List (Part 261, 40 CFR)
CFR	Code of Federal Regulations
DFTPP	Decafluorotriphenylphosphine
DNPH	Dinitrophenylhydrazine
DRE	Destruction and Removal Efficiency
EI	Electron Impact Ionization Mode
EPA	U.S. Environmental Protection Agency
g	Gram
GC	Gas Chromatography
GC/FID	Gas Chromatography/Flame-Ionization Detection
GC/MS	Gas Chromatography/Mass Spectrometry
h	Hour
HPLC	High-Performance Liquid Chromatography
HPLC/UV	High-Performance Liquid Chromatography/ Ultraviolet Spectrometry Detection
ID	Internal Diameter
is	Internal Standard
μg	Microgram (10^{-6} g)
μL	Microliter (10^{-6} g)
mg	Milligram (10^{-3} g)
mL	Milliliter (10^{-3} L)
mm	Millimeter (10^{-3} m)
MM5	Modified Method 5 Sampling Train
mol wt	Molecular Weight
ms	Millisecond
m/z	Mass to Charge Ratio
ng	Nanogram (10^{-9} g)
POHCs	Principal Organic Hazardous Constituents
QA	Quality Assurance
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
RRF	Relative Response Factor
RSD	Relative Standard Deviation
SASS	Source Assessment Sampling System
SIM	Selected-Ion Monitoring
s	Second
SD	Standard Deviation
SoRI	Southern Research Institute
t_r	Retention Time
UV	Ultraviolet Spectroscopy
VOST	Volatile Organic Sampling Train

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SECTION 1

INTRODUCTION

REGULATORY REQUIREMENTS FOR THE INCINERATION OF HAZARDOUS WASTES

As part of the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency (EPA) has promulgated proposed, interim, and final regulations for the owners and operators of facilities that treat hazardous wastes by incineration. The purpose of the regulations is to ensure that such incinerators are operated in an environmentally responsible manner. The regulations cover a range of activities, including operational performance standards, waste analysis, trial burns, monitoring and inspections, recordkeeping and reporting, and the establishment of emission-control criteria (1). The specific details for each incinerator facility are authorized by facility permits.

The primary criterion upon which all operational specifications are based is the destruction and removal efficiency (DRE) of the incinerator. This value, which is defined in terms of waste-input levels and stack-output levels of the potentially hazardous substances, must be greater than 99.99% for proper incineration. The substances from the list in Appendix VIII, Part 261, 40 CFR have been designated principal organic hazardous constituents (POHCs), although many inorganic substances have also been included.

SAMPLING AND ANALYTICAL METHODS FOR HAZARDOUS-WASTE INCINERATION

As part of the supporting documentation for the permit writer and for the incinerator facility's owners and operators, the EPA has compiled a manual of methods for sampling and analysis for use in measuring the levels of POHCs in the various streams of an incinerator facility, including inlet wastes, stack gas, process waters, fly ash, and bottom ash (2). This manual is entitled "Sampling and Analysis Methods for Hazardous Waste Combustion" and shall be referred to as the Methods Manual hereafter. This manual expands upon and augments the information in the "Guidance Manual for Evaluating Permit Applications for the Operation of Hazardous Waste Incineration Units" (3).

This Methods Manual is intended to be a resource document for the preparation and execution of a sampling-and-analysis plan for hazardous-waste incinerators. The specific procedures described are primarily in the form of brief descriptions with reference to other documents that contain highly detailed description methods. Existing collections of sampling and analysis methods documentation such as "Test Methods for Evaluating Solid Waste" (SW-846) or "Samplers and Sampling Procedures for Hazardous Waste Streams" (EPA-600/2-80-018) have not been directly incorporated into the manual but are incorporated by reference (4,5).

During trial burns at an incineration facility, the sampling and analysis methods will allow measurement of those POHCs expected to be present in the waste and products of incomplete combustion (PICs). Also during trial burns, the waste samples may be characterized with the methods to establish limits on the waste composition that may be incinerated. During routine facility operation, the incoming wastes will be analyzed periodically to ascertain whether the composition of the waste has changed. Some gaseous species such as carbon monoxide will be monitored continuously, as specified in the Methods Manual, as an indicator of the combustion efficiency of the process. Periodically, at the frequency not specified in the current regulations, the influent and effluent streams are to be tested to monitor compliance with the DRE criteria.

The overall strategy for waste characterization includes test procedures to determine the characteristics of the waste and analysis procedures to determine the composition of the waste. The Methods Manual includes test procedures for proximate, survey, and directed analysis. An overview of this analytical approach is shown in Figure 1. Our brief discussion here is limited to directed analysis because the modification of analytical methods applicable to the identification and quantitation of POHCs is presently of primary interest to us.

The directed-analysis portion of the waste-characterization scheme provides qualitative confirmation of compound identity and quantitative data with appropriate quality control for the potentially hazardous constituents that might reasonably be expected to be present in the waste, based on engineering judgment and on the results of proximate and survey analyses. Directed analysis does not involve screening every waste sample against the complete hazardous component list. A preliminary judgment is made as to the compounds or types of compounds that are likely to be present. The directed analysis then consists of the minimum set of analytical techniques that can be applied to the waste for qualitative identification and quantitative determination of the components that are actually present.

In practice, the results of the directed analysis will establish whether the waste contains the suspected pollutant and will demonstrate the concentration range at which the pollutant may be expected to be found. Directed analysis will also be used to confirm and quantify unexpected hazardous components identified in the survey analysis. These data on quantitative analysis of confirmed, identified contaminants of documented toxicity are essential for selection of appropriate POHCs to be monitored for the prediction of hazardous combustion by-products.

MODIFICATION OF DIRECTED-ANALYSIS METHODS

The Methods Manual recommends a variety of analytical techniques for the determination of the list of POHCs given in Appendix VIII, Part 261, 40 CFR. Whenever documentation was available to support the practice, the methods for the determination of organic compounds were written to incorporate a high-resolution analytical technique--fused-silica capillary gas chromatography--and a highly specific detection technique--mass spectrometry. Also, whenever

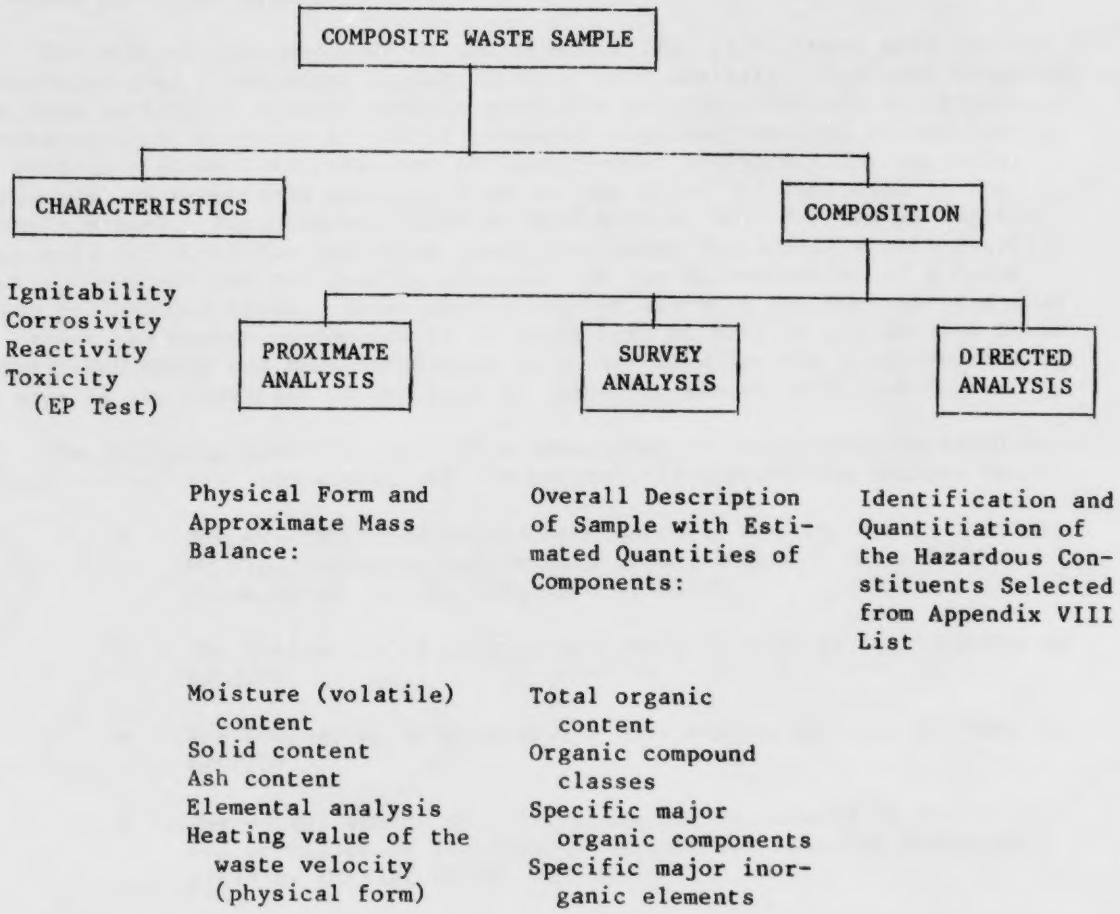
COMPOSITE WASTE SAMPLE
CHARACTERISTICS
COMPOSITION
Ignitability
Corrosivity
Reactivity
Toxicity
(EP Test)
PROXIMATE ANALYSIS
SURVEY ANALYSIS
DIRECTED ANALYSIS
Physical Form and Approximate Mass Balance:
Overall Description of Sample with Estimated Quantities of Components:
Identification and Quantitiation of the Hazardous Constituents Selected from Appendix VIII List
Moisture (volatile) content
Solid content
Ash content
Elemental analysis
Heating value of the waste velocity (physical form)
Total organic content
Organic compound classes
Specific major organic components
Specific major inorganic elements

FIGURE 1. Overview of the Analytical Approach for Waste Characterization.

possible, high-performance liquid chromatography (HPLC) was recommended for the determination of organic compounds that could not be determined by gas chromatography with mass spectrometric detection (GC/MS). Many compounds are amenable to analysis by either procedure. The application of these two approaches to the determination of as many of the POHCs as possible was designed to provide satisfactory qualitative analyses on a cost-effective basis for a variety of waste types and process chemistries.

For some of the compounds on the Appendix VIII list, there were limited references that recommended either GC/MS or HPLC analyses. For some compounds, the only analytical methods readily available were colorimetric or thin-layer chromatographic techniques. Other compounds required chemical derivatization to produce a product suitable for chromatographic analysis. For yet other compounds, no acceptable analytical method was found for inclusion in the Methods Manual. Furthermore, GC/MS or HPLC methods were documented for some compounds for which the operating conditions given for analysis were peculiar to the compounds and not readily adaptable to the determination of a broad range of compound types. Consequently, on the basis of the demonstrated need to reduce the number or complexity of analytical methods in the Methods Manual, generalized GC/MS and HPLC techniques were developed for the determination of as many of the chemicals on the list of hazardous wastes as possible.

The following specific tasks were undertaken to supplement the development of generalized test procedures and, in general, to improve the Methods Manual:

- The evaluation of generalized analysis methods for 51 POHCs by GC/FID. Based on information found, selected POHCs were recommended for determination by GC/MS.
- The evaluation of generalized analysis methods for 50 POHCs by HPLC/UV.
- The evaluation of generalized analysis methods for 48 POHCs by HPLC/UV.
- The establishment of calibration curves, limits of detection, and precision of recommended methods for selected POHCs determined by GC/FID, GC/MS, and HPLC/UV.
- The determination of the recovery of selected POHCs that were spiked at three concentration levels from Amberlite XAD-2 resin in sorbent tubes.

The subsequent sections of this report describe the efforts by Southern Research Institute to evaluate and, when necessary, modify GC/MS and HPLC/UV generalized analysis procedures for POHCs. This work is presented in Sections 4 and 5. The results of preliminary sorbent screening studies done on approximately 25 POHCs are presented in Section 6. And in Section 7 the GC/MS analysis of incinerator-effluent sample extracts is described.

SECTION 2

CONCLUSIONS

Generalized GC/FID, GC/MS, and HPLC/UV procedures were developed for the determination of approximately 100 candidate POHCs. The candidate POHCs represent a variety of compound types, including alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acids, aliphatic and aromatic amines, nitrated aromatics, nitrosoamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics.

The developed generalized methods are suitable for inclusion in the POHC Methods Manual. The methods were standardized with selected organic compounds over concentration ranges of interest and showed acceptable precision in the determination of most of the compounds.

Also, we showed that selected POHCs at low concentrations can be adsorbed on XAD-2 sorbent tubes and subsequently eluted efficiently for analysis by GC/MS or HPLC/UV. In this study, 25 POHCs were quantified by GC/MS, and 7 POHCs were quantified by HPLC/UV. In most instances, the averaged recovery was greater than 80%.

We applied the GC/MS survey method to the analysis of incinerator-effluent sample extracts. We were able to identify by retention times and mass spectra POHCs and other organic compounds. Our comparisons were made with a standard mixture of 156 POHCs, surrogate standards, and internal standard.

SECTION 3

RECOMMENDATIONS

Several recommendations for future investigations are as follows·

- SoRI will continue to apply the general survey methods to those 25 POHCs not yet evaluated. We have approximately 25 POHCs that should be screened for analysis. Additional work in 12 POHCs that were screened by SoRI is needed to find alternative chromatographic conditions for analysis.

- We now have at SoRI one class of compounds, aflatoxins, that should be screened by HPLC/UV and HPLC/fluorescence.

- Based on SoRI's findings, the proposed screening program should be evaluated when applied to incinerator-effluent samples, extracts, and sorbent media. Also, information is needed concerning the stability and storage of POHCs.

- In those cases where a generalized method was not sufficient to quantify a POHC, then more specific analytical techniques should be developed and evaluated on a priority basis.

SECTION 4

TECHNICAL APPROACH IN THE DEVELOPMENT OF GENERALIZED ANALYSIS METHODS

GENERAL CONSIDERATIONS

The primary focus of our experimental work was to develop two generalized analytical methods for the determination of POHCs in appropriate organic solvents. One analytical technique involved GC/MS with the use of a capillary column, and the other involved HPLC with ultraviolet/visible spectrophotometric detection (HPLC/UV).* During the optimization of the GC methods, flame-ionization detection (FID)--in addition to MS--was employed to aid in establishing operating conditions. The HPLC method was developed for use with reversed- phase C_{18} columns primarily because reversed-phase columns are less apt than normal-phase columns to adsorb organic analytes irreversibly. HPLC detection systems, other than ultraviolet/visible (UV/VIS) detector, were not considered because UV/VIS detection was judged to be more suitable for the development of a generalized HPLC test method. Because the UV/VIS detector can measure absorbances at selected wavelengths over a fairly broad range (190 to 600 nm), the detector offers selectivity and versatility in determining a variety of compound types.

The laboratory work was structured to lead systematically from the determination of the feasibility of developing generalized test methods to the standardization of the resulting methods for selected POHCs. First, we selected a variety of POHCs for preliminary investigation and performed analyses of standard solutions of mixtures of these POHCs (in appropriate solvents) to optimize instrumental operating conditions. Once suitable operating conditions had been established, an individual chromatogram for each of these POHCs was generated. Finally, we analyzed a series of standard solutions of each of the selected POHCs to estimate detection limits and to establish calibration curves. Also, multiple determinations were made on specific concentrations of selected POHCs to define the precision of the test methods.

Under another contract (Work Assignment 111, Contract 68-02-2685), we evaluated generalized GC/MS and HPLC/UV methods for the determination of approximately 70 candidate POHCs. The methods were calibrated for candidate organic compounds over concentration ranges of interest and demonstrated acceptable precision in the determination of most of the compounds. The candidate POHCs included alcohols, esters, chlorinated aliphatics and aromatics, carboxylic acid, aliphatic and aromatic amines, nitrated aromatics, nitrosamines, hydrazines, nitriles, organosulfur compounds, and polynuclear aromatics and heterocyclics.

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*Although the detector is capable of measuring absorbances in both the ultraviolet and visible regions (190 to 600 nm), we use the acronym HPLC/UV, which is conventional for describing HPLCs with variable-wavelength detectors.

The work described in this report is an extension of our previous Work Assignment under contract 68-02-2685. Not all of the candidate POHCs were submitted to proposed GC/MS and HPLC/UV analyses. Under this current Work Assignment, we have evaluated additional POHCs--50 for GC/MS and 48 for HPLC/UV. A detailed account of our findings is given in Section 5 of this report.

SELECTION OF CANDIDATE POHCs

We selected candidate POHCs for analysis by GC/FID, GC/MS, and HPLC/UV from the list of compounds in Appendix VIII, Part 261, 40 CFR. Those compounds listed as candidates under a generalized method were given first priority. From the initial list of 109 compounds, 28 were either not easily obtainable or were so hazardous that they would require special handling procedures. Of the remaining 81 compounds on the list for gas chromatography, we had 74 of them in our laboratory. From our available stock of chemicals, we screened 63 compounds by GC/FID to determine their retention times and response to the FID. The remaining 11 compounds from our laboratory stock were not screened because of their hazardous nature or their poor solubility in the solvent systems we selected for gas chromatography.

We also screened 53 compounds for HPLC/UV analysis.

PREPARATION OF STOCK STANDARD SOLUTIONS

We prepared stock standard solutions of the candidate compound in appropriate solvents at a concentration of either about 2 mg/mL or about 10 mg/mL. These stock solutions were serially diluted as required to prepare working standards.

We used either methylene chloride or methanol as the solvent in the preparation of standards for GC/MS studies. Several different polar solvents--acetonitrile, methanol, and water--were used in preparing solutions of POHCs determined by HPLC.

GC ANALYSIS PROCEDURES

Description of Instruments and General Operating Conditions

We developed the GC/MS generalized test method on the Hewlett-Packard Model 5985 gas chromatograph/mass spectrometer-data system. The components of the instruments include a hyperbolic quadrupole mass filter with a convertible electron-impact (EI) and positive-ion chemical-ionization source, a capillary and jet separator GC/MS interface, and a data system that includes an HP2113 computer, a high-speed printer, a magnetic tape system, a 50-megabyte HP7920M disk-drive system, a communications interface, GC/MS operating software, and an unabridged NBS spectral library. The supplemental GC/FID work was performed on a Hewlett-Packard Model 5840 gas chromatograph that was equipped for use with capillary columns.

The work with both GC/MS and GC/FID involved capillary column chromatography with matched, crosslinked fused-silica SE-54 capillary columns 25 m long, 0.31-mm ID. The initial operating conditions were chosen as a compromise of the conditions given for several capillary GC methods in the Methods Manual. The initial starting column temperature was 40 °C; the temperature was then programmed at 10 °C/min to 280 °C for 15 min. Injection and detection temperatures were 250 °C. The carrier gas was helium and was maintained at a volume flow rate through the column of about 2 mL/min. In both the GC/MS work and the GC/FID work, the "splitless" injection technique was employed. Consequently, we assumed that essentially all of the injected sample reached the column.

Optimization of the GC/FID and GC/MS Procedures

GC operating conditions were optimized by analyzing solutions containing a variety of the candidate POHCs by the GC/FID technique. The column-head pressure was adjusted appropriately to maximize the FID response to the test mixtures. We used these adjustments to pinpoint the optimum carrier-gas velocity.

Having established GC operating conditions by the GC/FID procedure, we then applied the method to the determination of the candidate POHCs by GC/MS. The mass spectrometer was operated in a full-mass-scanning range (41 to 450 amu) in the EI mode. The scan time was maintained at ≤ 1 s to enable the collection of enough scans to characterize each capillary GC peak.

GC Quality-Control Procedures

We calibrated the GC/FID and GC/MS procedures with external standard solutions of the candidate POHCs. Five-point to eight-point calibration curves were prepared for each candidate POHC determined by gas chromatography. Each curve was a plot of the FID or MS response (relative to anthracene-d_{10}) as a function of the quantity of the particular POHC injected on the GC column. The detection limit for each candidate POHC was estimated as the quantity (ng) of POHC on the GC column that gave rise to a signal approximately twice the background noise level. We also established reference mass spectra for the identification of the individual POHCs.

In addition to the use of external standards for the calibration of both GC/FID and GC/MS methods, other quality-control measures were implemented. The performance of the GC/MS system was checked daily with decafluorotriphenylphosphene (DFTPP) according to the requirements given in EPA Method No. 625 (6). The performance criteria listed in Table 1 were met.

The precision of determinations by GC/FID and GC/MS was estimated by triplicate injections of at least one standard solution of each POHC investigated by gas chromatography. The estimate of precision of the replicate measurements is expressed as the relative standard deviation (RSD) calculated from Equation 1.

TABLE 1. IONS AND ION ABUNDANCE CRITERIA OF DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

M/Z	Ion abundance criteria
51	30 to 60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40 to 60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5 to 9% of mass 198
275	10 to 30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17 to 23% of mass 442

$$\text{RSD}\ (\%) = \left(\frac{\text{SD}}{\overline{X}}\right) 100 \qquad (1)$$

Standard deviation (SD) was calculated from Equation 2.

$$\text{SD} = \sqrt{\frac{\sum_{i=1}^{n} (X_i - \overline{X})^2}{(n - 1)}} \qquad (2)$$

Mean relative response ($\overline{X}$) was calculated from Equation 3,

$$\overline{X} = \frac{1}{n} \sum_{i=1}^{n} X_i \qquad (3)$$

where

n = number of replicate measurements, and

X_i = relative response of the POHC standard.

Furthermore, we used anthracene-d_{10} as an internal standard in the GC methods. Along with the analytes we injected anthracene-d_{10} to minimize the effect of injection volume and instrument performance upon the precision of determinations. Also, the anthracene-d_{10} internal standard was used to calculate the relative response factor (RRF) for each POHC from Equation 4,

$$\text{RRF} = (A_s C_{is}) / (A_{is} C_s) \qquad (4)$$

where

A_s = area of the characteristic ion for the POHC to be measured,

A_{is} = area of the characteristic ion for the internal standard,

C_{is} = concentration of the internal standard (μg/mL), and

C_s = concentration of the POHC (μg/mL) to be measured.

Recovery data were not applicable for this phase of the project because our analyses were done with neat solutions and standard mixtures of POHCs. We did not collect, prepare, or analyze field samples that required spiking of the matrix with surrogate standards or specific POHCs.

HPLC/UV ANALYSIS PROCEDURES

For the development of a generalized HPLC/UV analysis procedure, we used the Hewlett-Packard Model 1084B high-performance liquid chromatograph equipped with a variable-wavelength UV/VIS detector (190 to 600 nm) and an automatic sampling system. The following two reversed-phase columns were used with an acetonitrile/water eluent:

- Perkin-Elmer HC-ODS-SIL-X-1, 10-μm particle size, 25 cm long, 2.6-mm ID.
- Waters Associates μBondapak C_{18}, 10-μm particle size, 30 cm long, 3.9-mm ID.

The μBondapak C_{18} column was employed only after we found that a few of the candidate POHCs either were not retained by or did not chromatograph well on the HC-ODS-SIL-X-1 column. In practice, the performance of a column from one source to another may vary. In addition, interlaboratory differences may occur that are attributed to the handling and history of the column. Once a column is selected, its performance should be monitored throughout the study.

Rather than attempt to establish one rigid set of HPLC operating conditions, our strategy was to identify various procedural options that would allow determination of a broad range of compound types. Thus, we investigated numerous isocratic and gradient elution programs with acetonitrile/water mobile phase. The wavelength of UV detection was also varied to optimize sensitivity.

Optimization and Calibration of the HPLC/UV Procedures

The POHCs were grouped into classes of compounds and submitted for HPLC analysis. Initially, we analyzed standard mixtures of candidate POHCs to establish solvent programs suitable for the determination of a variety of compounds. At that time the UV detector was set to monitor absorbances at 254 nm. Various chromatographic conditions were evaluated and modified until the elution rate and the resolution were optimized. The various procedures (options) are as follows:

Option 1--Perkin-Elmer HC-ODS-SIL-X-1, 10-μm particle size, 25 cm long x 2.6-mm ID

Option 1A--Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 5 min; 10 to 100% B in 35 min; 100% B, 10 min
Solvent Flow Rate: 1.0 mL/min

Option 1B--Solvent A: 1% (v/v) acetic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 10 min; 20 to 50% B in 10 min; 50% B, 5 min
Solvent Flow Rate: 2 mL/min

Option 1C--Solvent A: 1% (v/v) acetic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 2 min; 10 to 100% B in 18 min
Solvent Flow Rate: 2 mL/min

Option 1D--Solvent A: 0.1 M acetate buffer in distilled deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 2 min; 10 to 100% B in 18 min
Solvent Flow Rate: 1 mL/min

Option 1E--Solvent A: 0.005 M tetrabutylammonium phosphate in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 0 min; 20 to 100% B in 20 min
Solvent Flow Rate: 1 mL/min

Option 2--Waters Associates μBondapak C_{18}, 10-μm particle size, 30 cm long x 3.9-mm ID

Option 2A--Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 2% B, isocratic
Solvent Flow Rate: 1 mL/min

Option 2B--Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 10% B, 5 min; 10 to 100% B in 30 min
Solvent Flow Rate: 1 mL/min

Option 2C--Solvent A: Distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 0 min; 20 to 100% B in 20 min; 100% B, 10 min
Solvent Flow Rate: 1 mL/min

Option 2D--Solvent A: 0.01 M pentane sulfonic acid in distilled, deionized water
Solvent B: Acetonitrile
Solvent Program: 20% B, 10 min; 20 to 80% B in 20 min
Solvent Flow Rate: 1 mL/min

In subsequent work, the UV spectra of the candidate POHCs were determined on a Cary Model 17 spectrophotometer to establish an absorption maximum in the range from 190 to 400 nm that would be a suitable alternate wavelength for quantifying each POHC by HPLC/UV.

As in the GC/FID analyses, an eight-point calibration curve was prepared for each compound by plotting the absorbance as a function of the injected quantity of the compound. An internal standard was not used in the HPLC/UV determinations.

HPLC/UV Quality-Control Procedures

The precision of determinations by HPLC/UV was estimated by replicate injections (n = 5) of eight representative POHCs. An internal standard was not used in our HPLC/UV determinations. In practice, not all POHCs will be found in a sample. Thus, after the POHCs in the sample are identified, an appropriate internal standard can be selected and then added to improve the quantification of POHCs.

SECTION 5

RESULTS AND DISCUSSION OF THE DEVELOPMENT OF GENERALIZED ANALYSIS METHODS

GC/FID AND GC/MS ANALYSIS

General Considerations

In Table 2 we present a summary of the GC/FID determinations of candidate POHCs. The retention time and on-column detection limit are given for each compound. The compounds are listed in the order of their elution from the GC column. Retention times are relative to that observed for the internal standard, anthracene-d_{10}. The on-column detection limit is the quantity of each analyte that was estimated to yield an FID response of about twice the background signal. Typical values were 0.1 to 5.5 ng. Reference chromatograms and calibration curves, which appear in Appendix A, are also cited in Table 2.

Appendix A contains chromatograms of 16 different POHC mixtures. The chromatograms demonstrate the observed absolute retention times, the peak shapes, and any shifts in the base line that occurred during the analysis. Although no two of the candidate POHCs may coexist in a field situation and, therefore, may not require simultaneous determination, the chromatogram of the compound mixture demonstrates the resolving power of the capillary column in general.

Each reference calibration curve given in Appendix A and cited in Table 2 is a point-to-point plot (solid line) of the FID response as a function of the quantity of the analyte injected onto the GC column. Each plot can be used to estimate the sensitivity expected in the determination of a particular analyte. In generating these curves, we made no attempt to determine the upper limit of the linear range of determinations. However, each plot demonstrates the linearity of the FID response within the range of quantities investigated. A laboratory that uses these methods will have to generate its own calibration curves, which may differ slightly from the ones given in this report. Our calibration curves will serve as a guide.

Also, with each calibration curve is the least-squares plot (a broken line) based on the linear-regression analysis of FID response versus concentration of analyte. Linear-regression analysis of the data typically gave correlation coefficients of >0.9900.

In Table 3 we summarize the GC/MS determination of candidate POHCs. As in Table 2, the retention times are given relative to the internal standard, anthracene-d_{10}. Table 3 also lists the five most abundant mass fragments of each compound and, moreover, specifies the mass of the ion of each compound that was used for the establishment of detection limits and for the generation of calibration curves. The detection limits are the quantities of the analytes that were estimated to yield ion currents (of the selected ions) corresponding to about twice the background ion currents. Typical values of the detection limits were 0.1 to 7.7 ng.

TABLE 2. SUMMARY OF GC/FID DETERMINATIONS OF CANDIDATE POHCs

			Appendix A	
Compound	Relative retention times[a]	On-column detection limit[b] ,ng	Reference chromatogram	Reference calibration curve
Methyl methacrylate	0.111	0.1	A-52	A-53
Pyridine	0.124	0.1	A-61	A-62
2-Methyllactonitrile	0.139	0.2	A-47	A-48
Ethyl methacrylate	0.146	0.1	A-52	A-54
3-Chloropropionitrile	0.168	0.1	A-61	A-63
Ethyl carbamate	0.181	1.1	A-39	A-40
Methyl methanesulfonate	0.204	0.4	A-56	A-57
Benzenethiol	0.283	0.4	A-10	--
Aniline	0.298	0.2	A-6	A-7
2-Chlorophenol	0.308	0.2	A-13	A-14
o-Cresol	0.371	0.2	A-19	A-20
Acetophenone	0.384	0.7	A-1	A-2
p-Cresol	0.391	0.4	A-47	A-49
m-Cresol	0.395	0.5	A-52	A-55
α,α-Dimethylphenethylamine	0.425	0.1	A-61	A-64
(Dichloromethyl)benzene	0.456	0.1	A-56	A-58
2,4-Dimethylphenol	0.464	0.1	A-27	A-28
O,*O*,*O*-Triethyl phosphorothioate	0.479	0.4	A-6	A-8
o-Phenylenediamine	0.523	1.0	A-39	A-41
p-Phenylenediamine	0.577	3.2	A-1	A-3
p-Chloro-*m*-cresol	0.596	0.4	A-19	A-21
m-Phenylenediamine	0.605	2.1	A-39	A-42
2,4,6-Trichlorophenol	0.655	1.0	A-27	A-29
Isosafrole	0.677	1.1	A-44	A-45
Dimethyl phthalate	0.747	0.5	A-31	A-32
2-Naphthylamine	0.823	1.2	A-39	A-43
2,3,4,6-Tetrachlorophenol	0.823	0.8	A-13	A-15
Diethyl phthalate	0.858	0.1	A-31	A-33
4,6-Dinitro-*o*-cresol	0.874	0.2	A-19	A-22
Diphenylamine	0.880	0.4	A-37	A-38
Phosphorodithioic acid ester[c]	0.936	0.3	A-56	A-59
Diallate	0.938	0.2	A-24	A-25
Dimethoate	0.964	0.6	A-47	A-50
Octamethyl pyrophosphoramide	0.967	0.7	A-10	A-11
4-Aminobiphenyl	0.976	0.1	A-1	A-4
Pentachlorophenol	0.977	7.1	A-13	A-16
Pentachloronitrobenzene	0.991	0.1	A-13	A-17

(continued)

TABLE 2. (continued)

Compound	Relative retention times[a]	On-column detection limit[b], ng	Reference chromatogram	Reference calibration curve
Disulfoton	1.02	0.2	A-24	A-26
Methyl parathion	1.07	4.8	A-10	A-12
Dibutyl phthalate	1.12	0.6	A-31	A-34
Diisobutyl phthalate	1.12	0.2	A-19	A-23
Aramite	1.27	0.5	A-44	A-46
p-Dimethylaminoazobenzene	1.29	6.3	A-6	A-9
Chlorobenzilate	1.30	1.3	A-47	A-51
Kepone	1.32	0.2	A-1	A-5
Phosphorothioic acid ester[d]	1.34	3.2	A-56	A-60
Butylbenzyl phthalate	1.35	1.2	A-31	A-35
Methoxychlor	1.42	0.4	A-13	A-18
4,4'-Methylenebis-(2-chloroaniline)	1.42	1.6	A-61	A-65
Dioctyl phthalate	1.54	3.0	A-31	A-36
Hexachlorophene	1.63	1.1	A-27	A-30

[a] Relative to the retention time of anthracene-d_{10}; ≈16 min.

[b] Quantity required to yield a response twice the magnitude of the background signal.

[c] Phosphorodithioic acid, *O*,*O*-diethyl *S*-((ethylthio)methyl) ester.

[d] Phosphorothioic acid, *O*,*O*-dimethyl *O*-(*p*-((dimethylamino)sulfonyl)phenyl) ester.

TABLE 5. SUMMARY OF GC/MS DETERMINATIONS OF CANDIDATE POHSs

Compound	Relative retention time ^{a}	On-column detection limit,^{b} ng	Mol wt	Masses of characteristic EI ions (relative abundance)					Appendix B		
				1	2	3	4	5	Reference chromato-gram	Reference mass spectrum	Reference calibration curve
Methyl methacrylate	0.090	0.6	100	69(100)	100(58)	99(27)	41(27)	59(12)	B-91	B-92	B-93
Pyridine	0.119	0.5	79	79(100)	52(23)	78(13)	80(6)	53(2)	B-107	B-108	B-109
2-Methyllactonitrile	0.126	0.7	85	70(100)	69(6)	43(4)	71(4)	58(2)	B-91	B-94	B-95
Ethyl methacrylate	0.125	0.4	114	69(100)	99(29)	114(9)	70(5)	100(4)	B-82	B-83	B-84
3-Chloropropionitrile	0.160	0.3	89	89(100)	54(43)	91(28)	53(22)	52(9)	B-107	B-110	B-111
Ethyl carbamate	0.175	5.3	89	62(100)	44(92)	45(39)	74(34)	43(24)	B-68	B-69	B-70
Methyl methanesulfonate	0.190	0.8	110	79(100)	80(97)	95(26)	110(12)	65(12)	B-98	B-99	B-100
Benzenethiol	0.278	0.2	110	110(100)	109(26)	66(17)	111(8)	108(8)	B-17	B-18	B-19
Aniline	0.283	6.4	93	93(100)	66(26)	92(13)	65(12)	94(7)	B-10	B-11	B-12
2-Chlorophenol	0.292	0.5	128	128(100)	130(36)	64(36)	63(17)	91(14)	B-24	B-25	B-26
o-Cresol	0.356	0.6	108	108(100)	107(93)	79(22)	77(22)	90(19)	B-35	B-36	B-37
Acetophenone	0.377	0.6	120	105(100)	77(59)	120(40)	106(6)	78(6)	B-1	B-2	B-3
p-Cresol	0.392	0.5	108	107(100)	108(91)	109(7)	90(7)	91(3)	B-91	B-96	B-97
m-Cresol	0.378	0.3	108	108(100)	107(95)	79(25)	77(23)	90(11)	B-82	B-85	B-86
α,α-Dimethylphenethylamine	0.429	0.4	149	134(100)	72(19)	105(13)	135(10)	149(9)	B-107	B-112	B-113
(Dichloromethyl)benzene	0.453	0.3	160	125(100)	127(37)	160(17)	89(13)	162(11)	B-49	B-50	B-51
2,4-Dimethylphenol	0.448	0.5	122	122(100)	107(89)	121(50)	77(18)	91(15)	B-98	B-101	B-102
O,O,O-Triethyl phosphorothioate	0.469	0.5	198	198(100)	121(44)	97(24)	93(23)	115(21)	B-10	B-13	B-14
o-Phenylenediamine	0.527	0.6	108	108(100)	80(44)	107(24)	81(16)	53(10)	B-68	B-71	B-72
p-Phenylenediamine	0.567	2.0	108	108(100)	80(37)	107(27)	81(13)	53(9)	B-1	B-4	B-5
p-Chloro-m-cresol	0.585	0.9	142	142(100)	107(76)	144(34)	77(24)	143(14)	B-35	B-38	B-39
m-Phenylenediamine	0.606	0.6	108	108(100)	80(38)	81(23)	107(11)	53(6)	B-68	B-73	B-74
2,4,6-trichlorophenol	0.646	1.0	196	198(100)	196(96)	132(46)	97(41)	200(37)	B-49	B-52	B-53
Isosafrole	0.676	0.5	162	162(100)	131(37)	104(32)	161(29)	103(26)	B-77	B-78	B-79
Dimethyl phthalate	0.738	1.1	104	163(100)	194(15)	164(10)	77(7)	133(6)	B-54	B-55	B-56
2-Naphthylamine	0.824	0.5	143	143(100)	115(37)	116(16)	144(11)	142(6)	B-68	B-75	B-76
2,3,4,6-Tetrachlorophenol	0.820	3.4	230	232(100)	131(67)	230(67)	234(56)	55(44)	B-54	B-57	B-58
Diethyl phthalate	0.856	1.0	222	149(100)	177(24)	150(11)	176(11)	105(6)	B-35	B-40	B-41
4,6-Dinitro-o-cresol	0.869	7.5	198	198(100)	105(16)	121(11)	199(8)	168(8)	B-65	B-66	B-67

(continued)

TABLE 3 (continued)

Compound	Relative retention time[a]	On-column detection limit,[b] ng	mol wt	Masses of characteristic EI ions (relative abundance)					Appendix B		
				1	2	3	4	5	Reference chromatogram	Reference mass spectrum	Reference calibration curve
Diphenylamine	0.876	0.1	169	169(100)	168(75)	167(37)	170(15)	84(12)	B-65	B-66	B-67
Phosphorodithioic acid ester[c]	0.932	0.5	260	260(100)	75(93)	121(60)	231(46)	97(30)	B-98	B-103	B-104
Diallate	0.933	0.5	269	234(100)	236(38)	128(17)	235(15)	109(10)	B-44	B-45	B-46
Dimethoate	0.961	1.1	229	87(100)	93(51)	125(48)	143(18)	229(16)	B-82	B-87	B-88
Octamethyl pyrophosphoramide	0.968	3.4	286	153(100)	135(99)	199(95)	286(74)	243(67)	B-17	B-20	B-21
4-Aminobiphenyl	0.975	1.0	169	169(100)	168(23)	170(13)	167(13)	141(8)	B-1	B-6	B-7
Pentachlorophenol	0.977	3.7	264	266(100)	264(75)	268(63)	165(38)	130(38)	B-24	B-29	B-30
Pentachloronitrobenzene	0.992	3.6	293	295(100)	237(97)	249(82)	239(73)	214(67)	B-24	B-31	B-32
Disulfoton	1.02	2.1	274	88(100)	274(96)	89(43)	153(26)	142(24)	B-44	B-47	B-48
Methyl parathion	1.07	2.0	263	109(100)	125(74)	263(42)	79(28)	93(17)	B-17	B-22	B-23
Dibutyl phthalate	1.12	0.2	278	149(100)	150(9)	223(8)	205(6)	104(2)	B-54	B-59	B-60
Diisobutyl phthalate	1.12	6.7	278	149(100)	150(10)	223(9)	205(6)	104(3)	B-35	B-42	B-43
Aramite	1.27	6.4	334	185(100)	319(88)	191(62)	175(59)	187(50)	B-77	B-80	B-81
p-Dimethylaminoazobenzene	1.29	0.7	225	225(100)	120(48)	226(16)	148(12)	77(11)	B-82	B-89	B-90
Chlorobenzilate	1.29	1.5	324	251(100)	253(65)	139(54)	141(19)	111(17)	B-10	B-15	B-16
Kepone	1.33	5.0	270	272(100)	274(75)	270(50)	237(50)	235(42)	B-1	B-8	B-9
Phosphorothioic acid ester[d]	1.34	1.0	325	218(100)	217(19)	93(19)	125(17)	219(10)	B-98	B-105	B-106
Butylbenzyl phthalate	1.36	3.6	312	149(100)	91(44)	206(19)	132(13)	123(12)	B-54	B-61	B-62
Methoxychlor	1.43	0.5	344	227(100)	57(65)	44(59)	55(41)	56(29)	B-107	B-114	B-115
4,4'-Methylenebis(2-chloroaniline)	1.41	3.0	266	231(100)	266(98)	268(43)	195(32)	267(30)	B-24	B-33	B-34
Dioctyl phthalate	1.56	3.0	390	149(100)	43(12)	44(12)	150(10)	279(9)	B-54	B-63	B-64

[a] Relative to the retention time of anthracene-d_{10}; ≃16 min.

[b] Quantity required to yield a response twice the magnitude of the background signal.

[c] Phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester.

[d] Phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)sulfonyl)phenyl) ester.

Reference total-ion chromatograms, calibration curves, and mass spectra are cited in Table 3. The mass spectra are presented in Appendix B along with the reference chromatograms and calibration curves.

In Table 4 we present the results of triplicate GC/FID determinations of approximately 0.5-μg quantities of all of the candidate POHCs listed in Table 2. The calculated values of the standard deviation (SD) and relative standard deviation (RSD) in Table 4 indicate that most GC/FID determinations gave acceptable precision. None of the compounds gave an RSD greater than 12% except dioctyl phthalate, which was 13.9%. The averaged relative standard deviation was 5% ± 3.6%.

In Table 5 we present the results of triplicate GC/MS determinations of about 0.050-μg quantities of all of the POHCs listed in Table 3. In general, the GC/MS determinations were less precise than the GC/FID determinations. The averaged relative standard deviation was 9.2% ± 6%. The highest relative standard deviation, 27%, was given with octamethyl pyrophosphoramide.

POHCs Not Amenable to GC/FID and GC/MS Analysis

One compound, hexachlorophene, was not determined by GC/MS because it gave a low response. Even in the GC/FID determination, hexachlorophene gave a poor response to the flame-ionization detector. The compound may be decomposing in the injection port or on the column. At this time, we are unable to define the problem. Some of the compounds investigated could not be determined by the GC/FID or GC/MS survey methods. The retention time for methyl ethyl ketone was early for the generalized method that was established. By changing the chromatographic conditions, the volatile ketone can be quantified. Amitrole gave a very broad peak which causes the quantitation to be difficult. Under the suggested chromatographic conditions, hydrazine, Auramine O, propylamine, and propyleneimine did not elute from the column. These compounds may be unstable, or they may have reacted with the packing material in the column. Some compounds gave very poor responses, such as methyllactonitrile and 2,4-dithiobiuret. One compound, pronamide, co-eluted with the internal standard in the GC/FID method. This problem can be resolved by a different choice of internal standard.

TABLE 4. PRECISION OF GC/FID DETERMINATIONS

Compound	Quantity on column, ng	RRF[a]		
		Mean	SD	RSD, %
Acetophenone	515	1.04	0.031	3.0
4-Aminobiphenyl	525	0.671	0.0079	1.2
Aniline	477	0.993	0.032	3.2
Aramite	538	0.0951	0.0066	7.0
Benzenethiol	505	0.221	0.025	11
Butylbenzyl phthalate	630	0.206	0.022	10
Chlorobenzilate	467	0.302	0.020	6.7
p-Chloro-*m*-cresol	456	0.812	0.070	8.6
2-Chlorophenol	620	0.836	0.11	13
3-Chloropropionitrile	610	0.679	0.073	11
m-Cresol	612	1.890	0.16	8.7
o-Cresol	496	1.20	0.16	14
p-Cresol	466	0.897	0.057	6.3
Diallate	748	0.463	0.0053	11
Dibutyl phthalate	570	0.535	0.019	3.6
Dichloromethylbenzene	752	0.818	0.024	3.0
Diethyl phthalate	496	0.624	0.037	5.9
Diisobutyl phthalate	544	0.440	0.020	4.6
Dimethoate	421	0.16	0.0046	2.9
p-Dimethylaminoazobenzene	488	0.270	0.018	6.8
α,α-Dimethylphenethylamine	825	1.370	0.13	9.6
2,4-Dimethylphenol	515	0.982	0.020	2.0
Dimethyl phthalate	724	0.646	0.074	12
4,6-Dinitro-*o*-cresol	489	0.430	0.0074	1.7
Dioctyl phthalate	624	0.134	0.024	18
Diphenylamine	446	0.914	0.0055	0.60
Disulfoton	822	0.345	0.0025	0.73
Ethyl carbamate	476	0.388	0.012	3.2
Ethyl methacrylate	504	1.05	0.12	11
Hexachlorophene	530	0.0283	0.0054	19
Isosafrole	502	0.535	0.033	6.2
Kepone	295	0.0392	0.0026	6.5
Methoxychlor	510	0.160	0.0060	3.8
4,4'-methyllactonitrile-(2-chloroaniline)	585	0.104	0.012	12
2-Methyllactonitrile	710	0.555	0.048	8.6
Methyl methacrylate	704	1.01	0.12	12
Methyl methanesulfonate	854	0.294	0.010	3.5
Methyl parathion	456	0.261	0.017	6.4

(continued)

TABLE 4. (continued)

Compound	Quantity on column, ng	RRF[a] Mean	SD	RSD, %
2-Naphthylamine	314	0.897	0.054	6.1
Octamethyl pyrophosphoramide	585	0.270	0.016	6.1
Pentachloronitrobenzene	565	0.287	0.0036	1.3
Pentachlorophenol	465	0.254	0.0052	2.0
m-Phenylenediamine	592	0.769	0.039	5.0
o-Phenylenediamine	456	0.955	0.013	1.1
p-Phenylenediamine	505	0.733	0.012	1.7
Phosphorodithioic acid ester[b]	838	0.500	0.0057	1.1
Phosphorothioic acid ester[c]	764	0.105	0.011	11
Pyridine	585	1.400	0.15	11
2,3,4,6-Tetrachlorophenol	477	0.285	0.00094	3.3
2,4,6-Trichlorophenol	490	0.409	0.0081	2.0
O,*O*,*O*-Triethyl phosphorothioate	582	0.388	0.012	3.1

[a] Relative response factor = $(A_s C_{is})/(A_{is} C_s)$.

[b] Phosphorodithioic acid, *O*,*O*-diethyl *S*-((ethylthio)methyl) ester.

[c] Phosphorothioic acid, *O*,*O*-dimethyl *O*-(*p*-((dimethylamino)sulfonyl)phenyl) ester.

TABLE 5. PRECISION OF GC/MS DETERMINATIONS

Compound	Quantity injected, ng	RRF[a]		
		Mean	SD	RSD, %
Acetophenone	51.5	0.362	0.066	18
4-Aminobiphenyl	52.5	0.495	0.073	15
Aniline	47.7	0.432	0.0055	1.3
Aramite	53.8	0.0353	0.0034	9.5
Benzenethiol	50.5	0.0228	0.0013	5.7
Butylbenzyl phthalate	63.0	0.401	0.057	14
Chlorobenzilate	46.7	0.119	0.016	13
p-Chloro-m-cresol	45.6	0.217	0.038	18
2-Chlorophenol	62.0	0.349	0.032	9.0
3-Chloropropionitrile	61.0	0.0607	0.014	24
m-Cresol	61.2	0.467	0.039	8.3
o-Cresol	49.6	0.259	0.056	11
p-Cresol	46.6	0.399	0.042	11
Diallate	74.8	0.207	0.014	6.7
Dibutyl phthalate	57.0	1.490	0.20	14
Dichloromethylbenzene	50.2	0.407	0.048	12
Diethyl phthalate	49.6	1.00	0.12	12
Diisobutyl phthalate	54.5	1.57	0.14	8.9
Dimethoate	42.1	0.146	0.014	9.3
p-Dimethylaminoazobenzene	48.8	0.074	0.011	14
α,α-Dimethylphenethylamine	82.5	0.736	0.12	17
2,4-Dimethylphenol	51.5	0.234	0.025	11
Dimethyl phthalate	72.5	0.970	0.069	7.1
4,6-Dinitro-o-cresol	48.9	0.0225	0.00092	4.1
Dioctyl phthalate	62.5	0.829	0.0010	0.1
Diphenylamine	44.6	0.471	0.031	6.6
Disulfoton	82.2	0.0423	0.0072	17
Ethyl carbamate	47.6	0.961	0.012	13
Ethyl methacrylate	50.4	0.287	0.047	16
Isosafrole	50.2	0.228	0.014	5.9
Kepone	29.5	0.0798	0.015	19
2-Methyllactonitrile	71	0.406	0.044	11
Methyl methacrylate	70.4	0.190	0.017	8.8
Methyl methanesulfonate	57.0	0.132	0.030	23
Methyl parathion	45.6	0.254	0.026	10
Methoxychlor	51.0	0.327	0.018	5.7
2-Naphthylamine	31.4	0.671	0.0084	1.2

(continued)

TABLE 5. (continued)

Compound	Quantity injected, ng	RRF[a]		
		Mean	SD	RSD, %
Octamethyl pyrophosphoramide	58.5	0.129	0.037	29
Pentachloronitrobenzene	56.5	0.0452	0.0040	8.9
Pentachlorophenol	46.5	0.0656	0.0038	5.8
m-Phenylenediamine	59.2	0.320	0.024	7.6
o-Phenylenediamine	45.6	0.351	0.018	5.0
p-Phenylenediamine	50.5	0.133	0.022	16
Phosphorodithioic acid ester[b]	55.9	0.453	0.016	3.6
Phosphorothioic acid ester[c]	50.9	0.169	0.0097	5.8
Pyridine	58.5	0.354	0.099	28
2,3,4,6-Tetrachlorophenol	47.7	0.0423	0.0032	7.5
2,4,6-Trichlorophenol	49.0	0.169	0.0044	2.7
O,*O*,*O*-Triethyl phosphorothioate	58.2	0.187	0.0012	6.2

[a] Relative response factor $=(A_s C_{is})/(A_{is} C_s)$.

[b] Phosphorodithioic acid, *O*,*O*-diethyl *S*-((ethylthio)methyl) ester.

[c] Phosphorothioic acid, *O*,*O*-dimethyl *O*-(*p*-((dimethylamino)sulfonyl)phenyl) ester.

HPLC/UV ANALYSIS

General Considerations

We completed the determination of 48 POHCs by HPLC/UV. A summary of the results is given in Table 6. The retention time, on-column detection limit, and wavelength of detection are given for each POHC. The POHCs are listed in the order of their elution from the HPLC column and subdivided by procedural option. The on-column detection limit is the quantity of each POHC that was estimated to yield a UV absorbance of about twice the background signal. The wavelength of detection was 254 nm except where noted. An alternate wavelength was selected from the reference UV spectrum to optimize the detection of the POHC. Trypan blue gave maximum absorption in the visible spectra; therefore, this POHC was analyzed at 588 nm, which is in the VIS range. The VIS spectrum of Trypan blue is given in Figure C-78 of Appendix C.

Typical examples of HPLC/UV chromatograms and UV spectrum and standard calibration curves, which appear in Appendix C, are cross-referenced in Table 6. The chromatograms demonstrate the resolution and peak shape of each POHC, base-line drift, and any impurities or interferences present. Because of the probability of two unresolved POHCs coexisting in the same field situation, and, therefore, not requiring simultaneous determination, no attempt was made to resolve these POHCs. Should such a situation arise, a modification in the solvent programming or isocratic conditions may resolve the peaks.

The UV spectra presented in Appendix C give the relative absorbance of each POHC. From the maximum absorption, alternate wavelengths other than 254 nm may be selected to increase sensitivity or selectivity of each POHC.

Each reference calibration curve given in Appendix C and cited in Table 6 is a point-to-point plot (solid line) of recorded UV response as a function of the quantity of POHC on the HPLC column. This quantity was calculated from the injection volume and the standard concentration. The calibration curve is shown by a solid line. Also included on each graph is the plot of the linear-regression equation calculated from the standard-curve data. This plot is shown by a broken line. Linear-regression analysis typically yielded correlation coefficients in excess of 0.9999.

Each calibration curve can be used to estimate the sensitivity expected in the determination of a particular POHC. Each calibration curve demonstrates the linearity of response within the range of quantities investigated. We made no attempt to determine the upper limit of the linear range.

Table 7 presents the results of replicate (n = 5) HPLC determinations of 8 POHCs. The calculated values of the standard deviation (SD) and relative standard deviation (RSD) are given in the table. None of the compounds gave an RSD greater than 1.6%. The averaged RSD was 0.88%

TABLE 6. SUMMARY OF HPLC/UV DETERMINATION OF CANDIDATE POHCs

Compound	Procedural option[a]	Retention time, min	Wavelength of detection[b], nm	On-column detection limit[c], ng	Appendix C Reference HPLC chromatogram	Appendix C Reference UV spectrum	Appendix C Reference calibration curve
Maleic anhydride[d]	1A	1.5	254 / 210	6 / 0.4	C-1	C-2	C-3
N-methyl-*N'*-nitro-*N* nitrosoguanidine	1A	2.4	254 / 272	0.6 / 0.4	C-6	C-7	C-8
Phthalic anhydride[d]	1A	3.5	254 / 290	9 / 20	C-1	C-4	C-5
4-Nitroquinoline-1-oxide	1A	10.2	254 / 385	0.5 / 0.6	C-6	C-9	C-10
3-Methylphenol	1A	11.1	254 / 280	20 / 3	C-13 / C-14	C-15	C-16 / C-17
4-Methylphenol	1A	11.2	254 / 280	10 / 4	C-21 / C-22	C-23	C-24 / C-25
2-Methylphenol	1A	11.3	254 / 280	8 / 5	C-29 / C-30	C-31	C-32 / C-33
Phenacetin	1A	11.9	254 / 246	1 / 1	C-40	C-41	C-42
Melphalan	1A	13.3	254 / 260	1 / 1	C-45	C-46	C-47
2,4-Dimethylphenol	1A	15.3	254 / 280	20 / 1	C-21 / C-22	C-26	C-27 / C-28
2,6-Dichlorophenol	1A	15.8	254 / 280	10 / 1	C-13 / C-14	C-18	C-19 / C-20
Benzenethiol	1A	16.8	254 / 245	30 / 20	C-40	C-43	C-44
Formaldehyde[e]	1A	17.0	254 / 348	2 / 1	C-50	C-51	C-52
Acetaldehyde[e]	1A	19.2	254 / 359	2 / 1	C-50	C-53	C-54
2,4,5-Trichlorophenol	1A	20.3	254 / 280	8 / 2	C-29 / C-30	C-34	C-35 / C-36
Chloroacetaldehyde[e]	1A	20.6	254 / 352	4 / 2	C-57	C-58	C-59
Diethylstilbestrol	1A	20.8	254 / 240	0.6 / 0.4	C-6	C-11	C-12
Crotonaldehyde[e]	1A	23.0	254 / 375	2 / 1	C-50	C-55	C-56
Pentachlorophenol	1A	23.8	254 / 280	10 / 40	C-29 / C-30	C-37	C-38 / C-39
Benzaldehyde[e]	1A	24.7	254 / 378	40 / 0/7	C-45	C-48	C-49

(continued)

TABLE 6 (continued)

Compound	Procedural option[a]	Retention time, min	Wavelength of detection[b], nm	On-column detection limit[c], ng	Appendix C Reference HPLC chromatogram	Appendix C Reference UV spectrum	Appendix C Reference calibration curve
2,4-Dinitrophenol	1B	2.8	254 / 360	8 / 20	C-60	C-61	C-62
4,6-Dinitro-o-cresol	1B	6.8	254 / 360	20 / 50	C-60	C-63	C-64
Benzidine	1D	8.1	254 / 268	0.8 / 0.2	C-65	C-66	C-67
3,3'-Dimethoxybenzidine	1D	9.8	254 / 298	2 / 0.9	C-72	C-73	C-74
3,3'-Dimethylbenzidine	1D	10.0	254 / 288	0.9 / 0.2	C-65	C-68	C-69
o-Toluidine	1D	10.0	254 / 288	0.9 / 0.2	C-77	C-78	C-79
3,3'-Dichlorobenzidine	1D	12.5	254 / 280	2 / 0.7	C-72	C-75	C-76
4,4'-Methylene-bis(o-chloroaniline)	1D	12.7	254 / 298	0.6 / 2	C-65	C-70	C-71
Trypan blue	1E	8.2	588 / 315	20 / —	C-80	C-82 / C-81	C-83
Thiourea	2A	3.5	254 / 230	2 / 0.1	C-84	C-85	C-86
Thiosemicarbazide	2A	3.6	254 / 230	2 / 0.1	C-89	C-90	C-91
Azaserine	2A	3.6	254 / 280	0.2 / 0.3	C-94	C-95	C-96
Epinephrine	2A	4.5	254 / 280	1 / 0.1	C-96	C-97	C-98
Thioacetamide	2A	4.6	254 / 265	0.5 / 0.4	C-99	C-100	C-101
Ethylene thiourea	2A	4.8	254 / 242	4 / 1	C-86	C-89	C-90
1-Acetyl-2-thiourea	2A	5.6	254 / 272	0.8 / 0.3	C-81	C-84	C-85
Resorcinol	2A	8.6	254 / 280	3 / 0.7	C-91	C-94	C-95
Phenyl thiourea	2B	7.2	254 / 267	0.7 / 0.5	C-102	C-103	C-104
1-(o-Chlorophenyl)thiourea	2B	9.5	254 / 262	1 / 1	C-102	C-105	C-106
1-Naphthyl-2-thiourea	2B	15.5	254 / 290	0.8 / 1	C-102	C-107	C-108
Saccharin	2D	3.4	254 / 224	1 / 0.1	C-109	C-110	C-111
Streptozotocin	2D	3.4	254 / 230	0.4 / 0.3	C-114	C-115	C-116
Nicotine	2D	5.1	254 / 260	2 / 2	C-121	C-122	C-123
Mitomycin C	2D	5.6	254 / 363	1 / 0.3	C-128	C-129	C-130
Strychnine	2D	9.5	254 / 280	1 / 3	C-121	C-124	C-125
Brucine	2D	9.6	254 / 262	2 / 0.7	C-109	C-12	C-113
Methapyrilene	2D	18.2	254 / 302	0.8 / 2	C-121	C-126	C-127

Continued

TABLE 6 (continued)

Compound	Procedural option[a]	Retention time, min	Wavelength of detection[b], nm	On-column detection limit[c], ng	Appendix C Reference HPLC chromatogram	Appendix C Reference UV spectrum	Appendix C Reference calibration curve
Daunomycin	2D	21.9	254 / 233	0.3 / 0.2	C-117	C-120	C-121
4,4'-Methylene-bis(*o*-chloroaniline)	2D	24.2	254 / 298	0.3 / 1	C-117	C-122	C-123

[a] See Section 4, p. 12 for description of procedural options.

[b] The first wavelength given is the wavelength from which chromatogram and calibration curve were obtained. The second one is an alternate wavelength selected from the reference UV-VIS spectrum.

[c] Estimated quantity injected that is required to yield a response twice the magnitude of the background signal at the wavelength shown.

[d] The anhydride was determined as the acid.

[e] Derivatives were made with 2,4-dinitrophenylhydrazine according to Method A131 (2).

TABLE 7. PRECISION OF HPLC/UV DETERMINATIONS

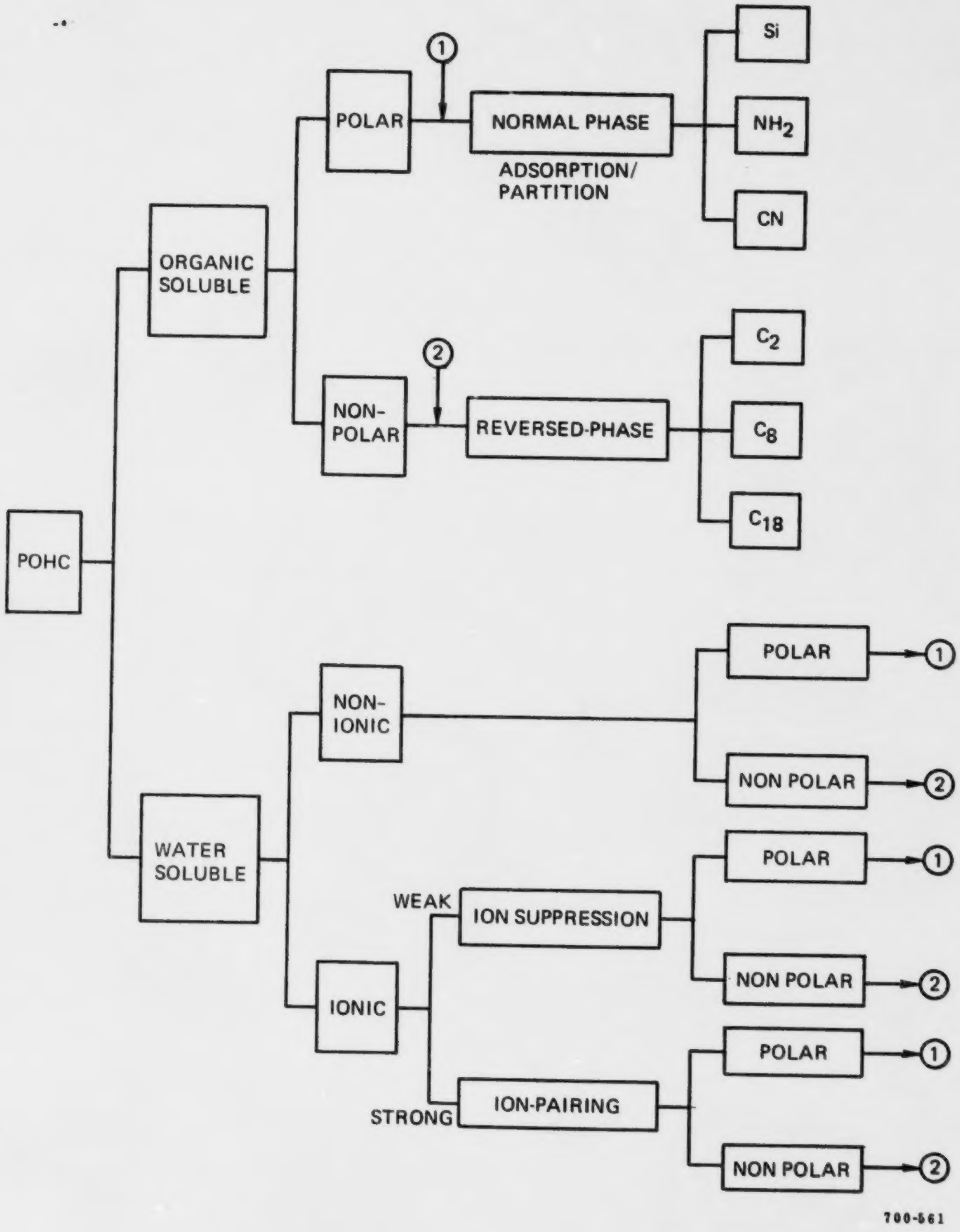
Compound	Quantity injected, µg	HPLC/UV response @254 nm, area counts x 10^{-3} Mean	SD	RSD, %
4-Nitroquinolin-1-oxide	1.0	585.1	8.1	1.4
4-Methylphenol	16	219.0	1.3	0.6
Melphalan	1.0	192.4	2.5	1.3
2,4-Dimethylphenol	8.0	110.1	0.8	0.7
2,6-Dichlorophenol	30	244.4	3.8	1.6
Formaldehyde	1.0	146.3	0.5	0.4
2,4,5-Trichlorophenol	5.0	52.6	0.3	0.5
Crotonaldehyde	1.0	126.9	0.6	0.5

HPLC/UV Methodology

A description of the generalized HPLC/UV analysis method including the various procedural options is presented in Section 4. p. 12. Figure 2 is a sorbent-selection guide for HPLC of a candidate POHC. Assuming that the POHC absorbs UV light, or can be made to do so, the schematic describes the route for the determination of most POHCs. For example, diethylstilbestrol (DES) is practically insoluble in water and is nonpolar. It can therefore be analyzed best by reversed-phase HPLC using a C_{18} column. N-Methyl-N'-nitro-N-nitrosoguanidine is much more polar than DES and would be best analyzed on one of the normal-phase columns. However, for the purposes of this study, we originally planned to analyze as many POHCs as possible by a generalized method using only one type of column (C_{18}) and one chromatographic technique (reversed-phase). This plan proved to be a very limiting approach. We therefore expanded the methodology to include other chromatographic conditions while still attempting to maintain the one-column type.

The first modification was the addition of acetic acid to the solvent system to suppress the formation of ionic species. Because reversed-phase chromatography achieves separation by different degrees of attraction of the sample for a nonpolar stationary phase and a polar-mobile phase, reversed-phase chromatography is most useful with nonpolar, nonionic compounds. To separate ionic compounds by reversed-phase, one must make these compounds behave as nonionic species with some nonpolar (lipophilic) characteristics. If the pH of these systems is adjusted with a buffer, the ionic/non ionic equilibrium is shifted toward the nonionic species. This technique is called ionic suppression and is used for weak acids and bases with buffers in the 2 to 8 pH range. The POHC, in its nonionic form, is then easily chromatographed. This was done in procedural options 1B and 1C. The same technique was used in Option 2D, with the addition of sodium acetate, buffered to a carefully controlled pH of 6.5. Sodium acetate was used rather than acetic acid because acetic acid gave a pH that was too low for the benzidines and similar structures to chromatograph well.

Stronger acids and bases, however, cannot be separated by this technique. They remain ionic in the 2 to 8 pH range and, thus, are poorly retained or elute as skewed peaks. A technique called ion-pair chromatography uses an organic counter-ion in the mobile phase that forms a reversible ion-pair complex with the ionized sample. This complex behaves as an electrically neutral (nonionic) and nonpolar compound. The extent to which the ionized sample and the counter-ion form an ion-pair complex and the relative size of the nonpolar group on the counter-ion will affect the degree of retention obtained. Pentane sulfonic acid, an alkyl sulfonate, was used as the counter-ion to complex with the basic drugs on Option 2D, whereas a quaternary amine, tetrabutylammonium phosphate, was used as the counter-ion to complex with the acidic Trypan Blue.



POHC
ORGANIC SOLUBLE
WATER SOLUBLE
POLAR
NON-POLAR
①
②
NORMAL PHASE
ADSORPTION/ PARTITION
REVERSED-PHASE
Si
NH2
CN
C2
C8
C18
NON-IONIC
IONIC
POLAR
NON POLAR
WEAK
STRONG
ION SUPPRESSION
ION-PAIRING
POLAR
NON POLAR
POLAR
NON POLAR
700-561

Figure 2. Sorbent-selection guide for column chromatography of POHCs.

POHCs Not Amenable to HPLC/UV Analysis

Six additional candidate POHCs were screened by HPLC/UV, by various procedural options, without success: chloral hydrate, cyclophosphamide, iron-dextran complex, metholymyl, 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, and paraldehyde (both in the native and DNPH-derivatized form). Chloral hydrate is the monohydrate of trichloroacetaldehyde and has the structure 2,2,2-trichloro-1,1-ethanediol. In the -diol form, chloral hydrate does not form a DNPH derivative nor does it absorb significantly UV/VIS light. Therefore, chloral hydrate cannot be analyzed by HPLC/UV unless the molecule is dehydrated to aldehyde form for derivatization. The anhydride and -diol may be resolved and quantified by alternative analyses.

Cyclophosphamide could not be determined reliably by the GC/FID or GC/MS survey methods. The compound was apparently irreversibly absorbed by the GC column or was decomposed in solution, on the column, or in the injection port. We also determined that the compound did not absorb appreciably UV/VIS light and, therefore, is not amenable to HPLC/UV analysis.

Iron-dextran complex does not lend itself to determination by any of the procedural options because of its high molecular weight and strong nonpolarity. The nonpolar C_{18} column retains the molecule almost permanently. An alternative route for investigation involves gel permeation or size-exclusion chromatography. In this technique, compounds are separated according to their effective size in solution by porous solids of various pore sizes. Small molecules permeate all the pores and are retained longer than large molecules which are excluded from the pores. The larger molecules therefore elute from the column before the small molecules.

Metholmyl belongs in the group of compounds referred to as oximes. Method A183 in the method manual may be the preferred analysis method as metholmyl does not appreciably absorb UV/VIS light (2). We believe the same to be true of 3,3-dimethyl-1-(methylthio)-2-butanone-O-[(methylamino)carbonoyl] oxime and 2-methyl-2-(methylthio)propionaldehyde-O-(methyl carbonyl) oxime.

The compound 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid was not available in the acid form but in the anhydride form. We expect that the anhydride, when mixed with water, will convert to the acid form and can be chromatographed. However, regardless of the form, the compound does not appreciably absorb UV/VIS light.

Paraldehyde is a trimer of acetaldehyde. It gives acetaldehyde on heating with dilute acid. We believe this occurs during the derivatization process and that we are seeing the derivative of acetaldehyde rather than of paraldehyde. The derivative of paraldehyde and acetaldehyde gives the same retention times and similar UV spectra. In addition, because of the lack of response to UV/VIS light, paraldehyde cannot be determined by HPLC/UV.

POHCs Not Available for HPLC/UV Analysis

We did not find a commercial source for the following eight POHCs: 2-*sec*-butyl-4,6-dinitrophenol, citrus red #2, cycasin, 2-cyclohexyl-4,6-dinitrophenol, ethylenebisdithiocarbamic acid, glycidylaldehyde, lasiocarpine, and uracil mustard. If these POHCs were made available, we believe they could be analyzed by HPLC/UV using one of the described procedural options.

Aflatoxins

No work was done on the determination of aflatoxins by HPLC/UV or HPLC/fluorescence because of the special safety precaution needed in handling the compounds. We expect minimal difficulty in performing such an analysis because of recent publications directed to this end.

HPLC Recommendations

As stated in the previous report, the μBondapak C_{18} was added to the method after we found a few of the POHCs either were not retained or did not chromatograph well on the HC-ODS-SIL-X-1 column. It was hoped that the increase in column size, and subsequent increase in packing, would retain the more polar compounds longer. After completion of the eight POHCs determined by Option 2A, we feel that these compounds, and four others, should be analyzed on a more polar reversed-phase column or on a normal-phase column. The other compounds include N-nitroso-N-methylurea, N-methyl-N'-nitro-N-nitrosoguanidine, saccharin, and streptozotocin.

If a third column is added to the method, we recommend that the remaining compounds analyzed by Method A123 be consolidated into Method A122 (2). This would be done by reanalyzing those compounds on the HC-ODS-SIL-X-1 column.

Option 1C should be eliminated from Method A122 because 4,6-dinitro-o-cresol has been analyzed using Option 1B.

Maleic and phthalic anhydride react readily with water to yield maleic and phthalic acid. Thus, it seems unlikely that the anhydrides would survive within stack-gas effluent streams because of the high concentration of water in the stream. We have reported the determination of the anhydride as the acid under Option 1A. If, however, the presence of the anhydride must be determined, the analysis must be done in an anhydrous environment. We therefore recommend that the anhydrides be chromatographed with a nonaqueous solvent system. We suspect that the more polar acid form will be retained longer than the comparitively less polar anhydride. Fractionation of the eluent and confirmation by other means is also recommended.

Derivatization of the aldehydes renders them responsive to UV light. The same is true of ketones. Therefore, we recommend that acetophenone, acrolein, acrylamide, and methyl ethyl ketone be determined by Method A132 in addition to Methods A101 and A121 (2).

Additional work needs to be done on the determination of chloroacetaldehyde by derivatization. Several impurity peaks were seen in the analysis that need to be identified or removed. We think they came from the bottle of chloroacetaldehyde. Perhaps a more pure source is available.

Three groups of compounds have recently been given much attention for analysis by HPLC. They are polynuclear aromatic hydrocarbons, phthalic acid esters, and chlorinated naphthalenes. Detection by fluorescence and UV absorption has been demonstrated. We recommend that this methodology be added to the existing work as an alternative to GC/FID or GC/MS.

Also, some organometallics may lend themselves to analysis by HPLC. Detection by UV, VIS, and fluorescence should be investigated.

SECTION 6

RECOVERY OF POHCs FROM AMBERLITE XAD-2 SORBENT TUBES

GENERAL CONSIDERATIONS

The sampling methods required for the ultimate analysis of POHCs in hazardous wastes and incinerator effluents during trial burns will vary according to the nature of the wastes. Prior to incineration, the hazardous waste may be a solid, liquid, slurry, or sludge. After incineration, the POHCs may be found in bottom ash, fly ash/ESP catches, scrubber water, or stack gas.

During trial burns, the measurement of POHCs in the stack-gas effluent is necessary for the calculation of DRE values to determine if the incinerator meets its performance criteria. The sampling of stack-gas components is most important to the process of obtaining permits for hazardous-waste incinerators. Some of the sampling methods available to collect volatile POHCs at low concentrations in stack gas are the Modified Method 5 (MM5) sampling train, the Source Assessment Sampling Systems (SASS), and the Volatile Organic Sampling Train (VOST). These systems use specific sorbents to collect POHCs. We selected XAD-2 resin, a general-purpose sorbent for organic compounds, to determine the recovery of POHCs from the sorbent.

SPIKING OF XAD-2 SORBENT TUBES

We prepared sorbent tubes as shown in Figure 3 by packing 400 mg of Amberlite XAD-2 resin in a 4-mm-ID Pyrex tube. The sorbent material was held in place by two silanized glass-wool plugs. A portion of a standard mixture containing ≈25 POHCs, internal standards, and surrogate standards was deposited on the sorbent. We spiked the sorbent tubes with POHCs at 10-, 30-, and 100-μg levels. Our internal standards were bromobenzene-d$_5$, aniline-d$_5$, phenol-d$_5$, nitrobenzene-d$_5$, naphthalene-d$_5$, biphenyl-d$_{10}$, acenaphthene-d$_{10}$, 2,4-dinitrophenol-d$_3$, phenanthrene-d$_{10}$, decafluorotriphenylphosphine, pyrene-d$_{10}$, chrysene-d$_{12}$, and benzo(a)pyrene-d$_{12}$. Our surrogate standards were 2-fluoroaniline, pentafluorophenol, and decafluorobiphenyl. The spiked sorbent tubes were sealed with end caps and stored for 1 to 72 hours before extraction with methylene chloride and subsequent analysis of the extract.

In addition, we established a laboratory exposure test that simulated the Source Assessment Sampling System (SASS) sampler. For this test we spiked selected POHCs, at the 100-μg level on 400-mg quantities of XAD-2 sorbent tubes as previously described. Then clean, moist air (≈85% humidity) was drawn at a flow of 1 L/min for 2 h through the sorbent tube. We extracted the exposed tube immediately with methylene chloride and analyzed the extract. All tests were performed three times. Prior to its use, the XAD-2 was cleaned by Soxhlet extraction with methylene chloride for 24 h. The sorbent was then dried under vacuum at 100 °C overnight.

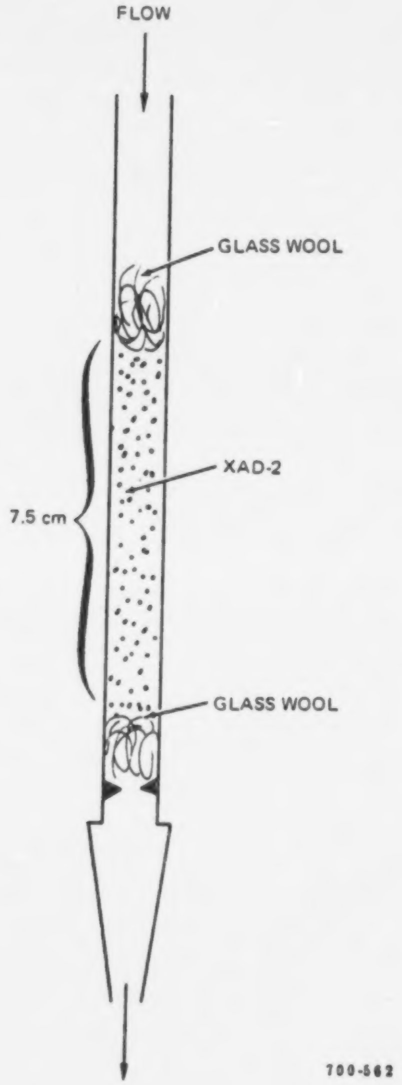

FLOW
GLASS WOOL
XAD-2
7.5 cm
GLASS WOOL
700-562

Figure 3. Drawing of sorbent-tube sampler for laboratory exposure test.

DESORPTION OF SORBENT TUBES

Each sorbent sample was transferred to a vial, ultrasonically extracted with 1 to 2 mL of methylene chloride for 10 min, and centrifuged. All extracts and the spiking solution were colored. An accurately measured volume (200 μL) was removed to a clean vial and analyzed.

ANALYSIS OF EXTRACTS

GC/MS Analysis

We found the following operating conditions to be optimum:

- Column: 25-m x 0.31-mm-ID fused-silica SE-54 capillary
- Injection-port temperature: 300 °C
- Carrier gas: Helium @ 20 cm/s
- Oven temperature: 40 °C for 4 min; programmed to 300 °C at 8 °C/min: held at 300 °C for 20 min
- Scan time: ≈1 s
- Start/stop masses: 40-350

HPLC/UV Analysis

We found the following operating conditions to be optimum:

- Column: HC-ODS-SIL-X-1(reversed-phase), 250 mm by 2.6-mm ID
- Solvent A: Distilled, deionized water
- Solvent B: Acetonitrile
- Solvent program: Isocratic elution employed for 5 min using 10% B, then gradient elution to 100% B over 35 min
- Solvent flow rate: 1 mL/min
- Detector UV, 254 nm
- Injection volume: 25 μL

DISCUSSION AND RESULTS

In our preliminary study on the recovery of 25 POHCs, we also included 13 internal standards and 3 surrogate standards. A list of these compounds with their masses of three key ions for GC/MS determinations is given in Table 8. An additional seven POHCs were analyzed by HPLC/UV and are listed in Table 9.

We do not intend to make conclusions based solely on the result of this study. However, certain trends can be ascertained from the data reported. For sorbent tubes spiked at the 10-μg level and analyzed by GC/MS, the average percent recovery based on the internal standard, phenanthrene-d_{10}, (excluding the diaminotoluenes) after 1-h equilibration interval was 80% (ranges of 73 to 101%). For the 30-μg spiking level, the average percent recovery was 114% (range of 87 to 151%). The summary of these data is in Tables 10 and 11. Sorbent tubes spiked at a 100-μg level and equilibrated for 1 h gave an average recovery of 110% (range of 86 to 143%). For an equilibration interval of 72 h, the average recovery was 103% (range of 81 to 116%). Summaries of recoveries for the 100-μg level are presented in Tables 12 and 13.

Also, we determined the recoveries of POHCs at the 100-μg spike level from XAD-2 sorbent tubes that were submitted to the laboratory exposure test. The results are reported in Table 14. The average percent recovery was 81% (range of 63 to 125%).

We repeated our recovery studies with those POHCs that could be determined by HPLC/UV analysis. Table 15 shows the average recovery of o-chlorophenol, reserpine, and chlorambucil at ≈10-, 30-, and 100-μg levels from XAD-2 sorbent after a 1-h equilibration interval. The average recovery was 99% (range of 85 to 105%). The average recovery of the same three POHCs spiked at the 100-μg level from XAD-2 sorbent tubes that were submitted to the laboratory exposure test was 95% (range of 91 to 103%). We reported these results in Table 16.

We have presented varying analytical data which indicate that test results may be influenced by the method used to quantitate these data. The average recovery of POHCs from the sorbent was determined both by the internal standard method (phenanthrene-d_{10} added prior to GC/MS analysis) and by the surrogate standards spiked in the sorbent tubes with the POHCs. We believe that these data are encouraging. They should be the foundation for the design of more comprehensive studies of sampling, sample preparation, and sample analysis in support of the program for incineration of hazardous waste.

TABLE 8. POHCS, INTERNAL STANDARDS, AND SURROGATE STANDARDS WITH MASSES OF THREE KEY IONS DETERMINED BY GC/MS

Compound	ID[a]	Masses of Characteristic EI Ions		
		1	2	3
N-Nitrosomethylethylamine		88	42	43
1,3-Dichloro-2-propanol		79	81	49
N-Nitrosodiethylamine		102	56	57
Bromobenzene-d_5	IS	82	161	163
Methanesulfonic acid, ethyl ester		79	109	97
2-Fluoraniline	SS	111	84	83
Pentachloroethane		117	119	167
Aniline-d_5	IS	98	70	71
Phenol-d_5	IS	99	71	71
Pentafluorophenol	SS	184	136	117
Benzyl chloride		91	92	126
N-Nitrosopyrrolidine		100	41	42
Nitrobenzene-d_5	IS	128	82	54
Decafluorobiphenyl	SS	265	334	335
Naphthalene-d_8	IS	136	135	108
2-6-Dichlorophenol		162	164	98
N-Nitrosodibutylamine		84	57	158
Safrole		162	131	104
3,4-Diaminotoluene		122	121	94
1,2,4.5-Tetrachlorobenzene		216	214	181
Nicotine		84	133	161
Trichlorophenol		198	196	134
Biphenyl-d_{10}	IS	164	162	82
2,4-Diaminotoluene		121	122	94
2,6-Diaminotoluene		122	121	94
Naphthoquinone		158	130	102
p-Dinitrobenzene		168	76	122
m-Dinitrobenzene		168	76	122
Acenaphthene-d_{10}	IS	164	162	82
2,4-Dinitrophenol-d_3	IS	187	157	66
Pentachlorobenzene		250	252	108
α-Naphthylamine		143	115	116
p-Nitroaniline		138	108	65
Phenanthrene-d_{10}	IS	188	187	94
Decafluorotriphenylphosphine	IS	198	255	77
Pyrene-d_{10}	IS	212	208	108
2-Acetylaminofluorene		181	223	152
Chrysene-d_{12}	IS	240	241	120
9,10-Dimethyl(*1*,*2*)benzanthracene		256	257	241
Benzo[a]pyrene-d_{12}	IS	264	265	280
Dibenz[a,j]acridine		279	277	280

[a] IS = internal standard; SS = surrogate standard

TABLE 9. POHCS DETERMINED BY HPLC/UV

Compound
Reserpine
3-(α-Acetonylbenzyl)-4-hydroxycoumarin
Chlorambucil
Tetramethylthiuram disulfide
2,3,4,6-Tetrachlorophenol
2,4,6-Trichlorophenol
o-Chlorophenol

TABLE 10. AVERAGE RECOVERY OF POHCS FROM XAD-2 AT ≈10 μg AFTER 1-h EQUILIBRATION; GC/MS ANALYSIS

Compound	Amount added, μg	Amount found. μg	Recovery,[a] %			
			A	B	C	D
N-Nitrosomethylethylamine	9.8	6.5	66.3	61.4	90.8	53.5
1.3-Dichloro-2-propanol	9.0	6.7	74.4	68.9	102	60.0
N-Nitrosodiethylamine	9.7	9.0	92.8	85.9	127	74.8
Methanesulfonic acid, ethyl ester	9.1	8.3	90.8	84.1	124	73.2
Pentachloroethane	11	9.3	82.3	76.2	113	66.4
Benzyl chloride	8.3	7.3	87.4	80.9	120	70.5
N-Nitrosopyrrolidine	13	23	183	169	251	147
2,6-Dichlorophenol	8.6	6.8	78.9	73.1	108	63.6
N-Nitrosodibutylamine	9.9	8.6	87.1	80.6	119	70.2
Safrole	7 9	6.3	79.8	73.9	109	64.4
3,4-Diaminotoluene	11	--[b]	--	--	--	--
1.2,4,5-Tetrachlorobenzene	7.9	7.1	90.3	83.6	124	72.8
Nicotine	9.2	7.6	82.6	79.5	113	66.6
Trichlorophenol	8.3	7.6	91.8	85.0	126	74.0
2,4-Diaminotoluene	11	--	--	--	--	--
2,6-Diaminotoluene	9.8	--	--	--	--	--
Naphthoquinone	5.4	--	--	--	--	--
p-Dinitrobenzene	10	10	101	93.5	138	81.5
m-Dinitrobenzene	7.6	7.2	95.2	88.1	130	76.8
Pentachlorobenzene	8.4	6.2	74.3	68.8	102	59.9
α-Naphthylamine	8.1	4.8	59.0	54.6	80.8	47.6
p-Nitroaniline	11	8.6	80.4	74.4	110	64.8
2-Acetylaminofluorene	7.7	5.6	73.4	68.0	100	59.2
9,10-Dimethyl(1 2)benzanthracene	5.9	5.3	89.1	82.5	122	71.9
Dibenz[a,j]acridine	5.3	4.5	85.4	79.1	117	68.9

[a] Relative to (A) phenanthrene-d_{10}, (B) 2-fluoraniline.(C) pentafluorophenol, and (D) decafluorobiphenyl.

[b] Amount found was not determined because peaks were asymmetrical and poorly resolved.

TABLE 11. AVERAGE RECOVERY OF POHCS FROM XAD-2 AT ≈30 μg AFTER 1-h EQUILIBRATION; GC/MS ANALYSIS

Compound	Amount added, μg	Amount found, μg	Recovery,[a] %			
			A	B	C	D
N-Nitrosomethylethylamine	29	43.8	151	114	134	114
1,3-Dichloro-2-propanol	27	36.8	136	102	120	103
N-Nitrosodiethylamine	29	39.4	136	102	120	103
Methanesulfonic acid, ethyl ester	27	35.6	132	99.2	117	100
Pentachloroethane	34	42.0	124	93.2	109	93.9
Benzyl chloride	25	32.7	131	98.5	116	99.2
N-Nitrosopyrrolidine	38	50.8	134	101	119	102
2,6-Dichlorophenol	26	33.0	127	95.5	112	96.2
N-Nitrosodibutylamine	30	39.1	130	97.7	115	98.4
Safrole	24	31.9	133	100	118	101
3,4-Diaminotoluene	32	7.47	23.3	17.5	20.6	17.7
1,2,4,5-Tetrachlorobenzene	24	31.7	132	99.2	117	100
Nicotine	28	34.8	124	93.2	110	93.9
Trichlorophenol	25	28.4	114	85.7	101	86.3
2,4-Diaminotoluene	32	0.7	2.2	1.7	1.9	1.7
2,6-Diaminotoluene	29	22.2	76.4	57.4	67.6	57.9
Naphthoquinone	16	23.2	145	109	128	110
p-Dinitrobenzene	31	40.4	130	97.7	115	98.5
m-Dinitrobenzene	23	29.1	127	95.5	112	96.2
Pentachlorobenzene	25	29.0	116	87.2	103	87.9
α-Naphthylamine	24	27.3	114	85.7	101	86.4
p-Nitroaniline	32	34.7	109	82.0	96.5	82.6
2-Acetylaminofluorene	23	24.5	107	80.4	94.7	81.1
9,10-Dimethyl(1,2)benzanthracene	18	17.6	97.5	73.3	86.3	73.9
Dibenz[a,j]acridine	16	13.9	86.7	65.2	76.7	65.7

[a] Relative to (A) phenanthrene-d_{10}, (B) 2-fluoraniline, (C) pentafluorophenol, and (D) decafluorobiphenyl.

TABLE 12. AVERAGE RECOVERY OF POHCS FROM XAD-2 AT ≃100 μg AFTER 1-h EQUILIBRATION; GC/MS ANALYSIS

Compound	Amount added, μg	Recovery, %, relative to															
		phenanthrene-d_{10}				2-fluoroaniline				pentafluorophenol				decafluorobiphenyl			
		1	2	3	Avg	1	2	3	Avg	1	2	3	Avg	1	2	3	Avg
N-Nitrosomethylethylamine	98	99.3	112	137	116	87.1	88.2	88.4	87.9	60.5	77.3	85.1	74.3	77.6	80.6	85.1	81.1
1,3-Dichloro-2-propanol	90	98.8	111	131	114	86.7	87.4	84.5	86.2	60.2	71.6	81.4	71.1	72.2	79.9	81.4	77.8
N-Nitrosodiethylamine	97	101	108	126	112	88.0	85.0	81.3	84.8	61.6	69.7	78.3	69.9	78.9	77.7	78.3	78.3
Methanesulfonic acid, ethyl ester	91	97.9	73.8	85.3	85.7	85.9	58.1	55.0	66.3	59.7	47.6	53.0	53.4	76.5	53.1	53.0	60.9
Pentachloroethane	113	97.3	104	127	109	85.4	81.9	81.9	83.1	59.3	67.1	78.9	68.4	76.0	74.8	78.9	76.6
Benzyl chloride	83	90.5	105	124	106	79.4	82.7	80.0	80.7	55.2	67.7	77.0	66.6	70.7	75.5	77.0	74.4
N-Nitrosopyrrolidine	127	101	111	128	113	88.6	87.4	82.6	86.2	61.6	71.6	79.5	70.9	78.9	79.9	79.5	79.4
2,6-Dichlorophenol	86	97.1	106	117	107	85.2	83.5	75.5	81.4	59.2	68.4	72.7	66.8	75.9	76.3	72.7	75.0
N-Nitrosodibutylamine	99	101	112	119	111	88.6	88.2	76.8	84.5	61.6	72.3	73.9	69.3	78.9	80.6	73.9	77.8
Safrole	79	98.6	106	123	109	86.5	83.5	79.4	83.1	60.1	68.4	76.4	68.3	77.0	76.3	76.4	76.6
3,4-Diaminotoluene	105	91.6	85.6	80.4	85.9	80.4	67.4	51.9	66.6	55.9	55.2	49.9	53.7	71.6	61.6	49.9	61.0
1,2,4,5-Tetrachlorobenzene	79	92.8	103	114	103	81.4	81.1	73.5	78.7	56.6	66.4	70.8	64.6	72.5	74.1	70.8	72.5
Nicotine	92	102	117	141	120	89.5	92.1	91.0	90.9	62.2	75.5	87.6	75.1	79.7	84.2	87.6	83.8
Trichlorophenol	83	97.7	107	116	107	85.7	84.3	74.8	81.6	59.6	69.0	72.0	66.9	76.3	77.0	72.0	75.1
2,4-Diaminotoluene	105	107	105	97.1	103	93.9	82.7	62.6	79.7	65.2	67.7	60.3	64.4	83.6	75.5	60.3	73.1
2,6-Diaminotoluene	98	109	108	98.7	105	95.6	85.0	63.7	81.4	66.5	69.7	61.3	65.8	85.2	77.7	61.3	74.7
Naphthoquinone	54	93	82.4	124	99.8	81.6	65.0	80.0	75.5	56.7	53.2	77.0	62.3	75.7	59.4	77.0	70.7
p-Dinitrobenzene	103	105	113	123	114	92.1	89.0	79.4	86.8	64.0	72.9	76.4	71.1	82.0	81.3	76.4	79.9
m-Dinitrobenzene	76	108	115	118	114	87.7	90.6	76.1	84.8	65.9	74.2	73.3	71.1	84.4	82.7	73.3	80.1
Pentachlorobenzene	84	96.9	103	112	104	85.0	81.1	72.3	79.5	59.1	66.5	69.6	65.1	75.7	74.1	69.6	73.2
α-Naphthylamine	81	109	117	120	115	95.6	92.1	77.4	88.4	66.5	75.5	74.5	72.2	85.2	84.2	74.5	81.3
p-Nitroaniline	107	115	116	123	118	101	91.3	79.4	90.5	70.1	74.8	76.4	73.8	89.8	83.5	76.4	83.2
2-Acetylaminofluorene	77	165	124	110	133	145	97.6	71.0	104.4	01	80.0	68.3	83.0	129	89.2	68.3	95.5
9,10-Dimethyl(1,2)benzanthracene	59	130	110	99.0	113	114	86.6	63.9	88.2	79.3	71.0	61.5	70.6	102	79.1	61.5	80.7
Dibenz[a,j]acridine	53	186	130	112	143	163	102	105	123	13	83.9	101	99.5	145	93.5	101	113

TABLE 13. AVERAGE RECOVERY OF POHCS FROM XAD-2 AT ≃100 µg AFTER 72-h EQUILIBRATION; GC/MS ANALYSIS

Compound	Amount added, µg	Recovery, %, relative to															
		phenanthrene-d_{10}				2-fluoroaniline				pentafluorophenol				decafluorobiphenyl			
		1	2	3	Avg	1	2	3	Avg	1	2	3	Avg	1	2	3	Avg
N-Nitrosomethylethylamine	98	90.7	130	106	109	82.5	82.8	85.5	83.6	75.0	75.6	80.3	77.0	78.2	83.3	73.1	78.2
1,3-Dichloro-2-propanol	90	79.6	112	97.2	96.5	72.4	71.3	78.4	74.0	65.8	65.1	73.6	68.2	68.6	71.8	67.0	69.1
N-Nitrosodiethylamine	97	80.8	118	98.2	99.0	73.5	75.2	79.2	76.0	66.8	68.0	74.4	69.7	69.7	75.6	67.7	71.0
Methanesulfonic acid, ethyl ester	91	85.6	123	102	104	77.8	78.3	82.3	79.5	70.7	71.5	77.3	73.2	73.8	78.8	70.3	74.3
Pentachloroethane	113	86.5	115	95.5	99.0	78.6	73.2	77.0	76.3	71.5	66.9	72.3	70.2	74.6	73.7	65.9	71.4
Benzyl chloride	83	87.8	119	101	103	79.7	75.8	81.5	79.0	72.5	69.2	76.5	72.7	75.6	76.3	69.7	73.9
N-Nitrosopyrrolidine	127	96.1	133	103	111	87.4	84.7	83.1	85.1	79.4	77.3	78.0	78.2	82.8	85.3	71.0	79.7
2,6-Dichlorophenol	86	96.5	125	108	110	87.7	79.6	87.1	84.8	79.8	72.7	81.8	78.1	83.1	80.1	74.5	79.2
N-Nitrosodibutylamine	99	105	131	112	116	95.5	83.4	90.3	89.7	86.8	76.1	84.8	82.6	90.5	84.0	77.2	83.9
Safrole	79	98.1	126	104	109	89.2	80.3	83.9	84.5	81.1	73.3	78.8	77.7	84.6	80.8	71.7	79.0
3,4-Diaminotoluene	105	27.0	29.0	26.6	27.5	24.5	18.5	21.5	21.5	22.3	16.9	20.2	19.8	23.3	18.6	18.3	20.1
1,2,4,5-Tetrachlorobenzene	79	91.0	116	105	104	82.7	73.9	84.7	80.4	75.2	67.4	79.5	74.0	78.4	74.4	72.4	75.1
Nicotine	92	96.6	117	112	109	87.8	74.5	90.3	84.2	79.8	68.0	84.8	77.5	83.3	75.0	77.2	78.5
Trichlorophenol	83	95.9	114	96.9	102	87.2	72.6	78.1	79.3	79.3	66.3	73.4	73.0	82.7	73.1	66.8	74.2
2,4-Diaminotoluene	105	1.5	1.7	0.96	1.39	1.4	1.1	0.77	1.09	1.4	0.99	0.72	1.04	0.83	1.09	0.66	0.86
2,6-Diaminotoluene	98	45.3	51.7	45.4	47.5	41.2	32.9	36.6	36.9	37.4	30.1	34.4	34.0	39.1	33.1	31.3	34.5
Naphthoquinone	54	71.1	92.4	80.7	81.4	64.6	58.9	65.1	62.9	58.8	53.7	61.1	57.9	61.3	59.2	55.7	58.7
p-Dinitrobenzene	103	106	118	102	109	96.4	75.2	82.3	84.6	87.6	68.6	77.3	77.8	91.4	75.6	70.3	79.1
m-Dinitrobenzene	76	109	115	105	110	99.1	73.2	84.7	85.7	90.1	66.9	79.5	78.8	94.0	73.7	72.4	80.0
Pentachlorobenzene	84	95.5	114	103	104	86.8	72.6	83.1	80.8	78.9	66.3	78.0	74.4	82.3	73.1	71.0	75.5
α-Naphthylamine	81	107	112	102	107	97.3	71.3	82.3	83.6	88.4	65.1	77.3	76.9	92.2	71.8	70.3	78.1
p-Nitroaniline	107	93.3	102	89.9	95.1	84.8	65.0	72.5	74.1	77.1	59.3	68.1	68.2	80.4	65.4	62.0	69.3
2-Acetylaminofluorene	77	103	95.9	96.6	98.5	93.6	61.1	77.9	77.5	85.1	55.8	73.2	71.4	88.8	61.5	66.6	72.3
9,10-Dimethyl(1,2)benzanthracene	59	82.5	88.3	92.3	87.7	75.0	56.2	74.4	68.5	68.0	51.3	69.9	63.1	71.7	56.6	63.7	64.0
Dibenz[a,j]acridine	53	90.9	116	82.6	96.5	82.6	73.9	66.6	74.4	75.1	67.4	62.6	68.4	78.4	74.4	57.0	69.9

TABLE 14. AVERAGE RECOVERY OF POHCS FROM XAD-2 AFTER LABORATORY EXPOSURE TEST; GC/MS ANALYSIS

Compound	Amount added, µg	Recovery, %, relative to															
		phenanthrene-d_{10}				2-fluoroaniline				pentafluorophenol				decafluorobiphenyl			
		1	2	3	Avg	1	2	3	Avg	1	2	3	Avg	1	2	3	Avg
N-Nitrosomethylethylamine	98	83.5	52.1	55.8	63.8	73.2	65.4	75.4	71.3	62.8	47.8	61.5	57.4	70.2	62.4	67.5	66.7
1,3-Dichloro-2-propanol	90	93.6	60.0	58.0	70.5	82.1	75.2	78.3	78.5	70.3	55.0	63.9	63.1	78.7	71.9	70.1	73.6
N-Nitrosodiethylamine	97	98.7	56.5	56.8	70.7	86.6	71.3	76.8	78.2	74.2	51.8	62.6	62.9	82.9	67.7	68.9	73.2
Methanesulfonic acid, ethyl ester	91	104	67.1	60.5	77.2	91.2	75.9	81.8	83.0	78.2	61.6	66.6	68.8	87.4	80.4	73.2	80.3
Pentachloroethane	113	74.8	55.0	53.6	61.1	65.6	67.3	72.4	68.4	56.2	50.5	59.0	55.2	62.9	65.9	64.8	64.5
Benzyl chloride	83	88.7	60.8	59.8	69.8	77.8	75.0	80.5	77.8	66.7	55.8	65.9	62.9	74.5	72.8	72.3	73.2
N-Nitrosopyrrolidine	127	120	76.6	66.7	87.8	105	83.7	90.1	92.9	90.2	70.3	73.5	78.0	101	91.7	80.7	91.1
2,6-Dichlorophenol	86	109	78.7	68.2	85.3	95.6	98.7	92.2	95.5	82.0	72.2	75.1	76.4	91.6	94.3	82.5	89.5
N-Nitrosodibutylamine	99	115	79.6	73.9	89.5	101	99.9	99.9	100	86.5	73.0	81.4	80.3	96.6	95.3	89.4	93.8
Safrole	79	104	72.4	71.1	82.5	91.2	90.8	96.1	92.7	78.2	66.4	78.3	74.3	87.4	86.7	86.0	86.7
3,4-Diaminotoluene	105	49.2	16.4	17.5	27.7	43.2	20.6	23.6	29.1	37.0	15.0	19.3	23.8	41.3	19.6	21.2	27.4
1,2,4,5-Tetrachlorobenzene	79	104	66.1	63.9	78.0	91.2	82.9	86.4	86.8	78.2	60.6	70.4	69.7	87.4	79.2	77.3	81.3
Nicotine	92	102	75.5	57.2	78.2	89.5	94.7	77.3	87.2	76.7	69.2	63.0	69.6	85.7	90.4	69.2	81.8
Trichlorophenol	83	101	78.1	64.9	81.3	88.6	98.0	87.7	91.4	75.9	71.7	71.5	73.0	84.9	93.5	78.5	85.6
2,4-Diaminotoluene	105	110	9.4	8.8	42.7	96.5	11.8	11.9	40.1	82.7	8.6	9.7	33.7	92.4	11.3	10.6	38.1
2,6-Diaminotoluene	98	111	47.1	46.0	68.0	97.4	59.1	62.2	72.9	83.5	43.2	50.7	59.1	93.3	56.4	55.6	68.4
Naphthoquinone	54	133	77.4	77.0	95.8	117	97.1	104	106	100	71.0	84.8	85.3	112	92.7	93.1	99.2
p-Dinitrobenzene	103	117	83.8	73.7	91.5	102	105	99.6	102	88.0	76.9	81.2	82.0	98.3	100	89.1	95.9
m-Dinitrobenzene	76	116	90.5	74.6	93.7	102	114	101	106	87.2	83.0	82.2	84.1	97.5	108	90.2	98.7
Pentachlorobenzene	84	100	76.8	69.8	82.2	87.7	96.4	94.3	92.8	75.2	70.5	76.9	74.2	84.0	92.0	84.4	86.6
α-Naphthylamine	81	103	91.9	76.4	90.4	90.4	115	103	103	77.4	84.3	84.1	81.9	86.6	110	92.4	96.4
p-Nitroaniline	107	99.1	96.3	71.9	86.9	89.1	121	97.1	102	74.5	88.3	79.2	80.7	83.3	115	86.9	95.2
2-Acetylaminofluorene	77	75.6	128	135	113	66.3	161	182	136	56.8	117	149	108	63.5	153	163	127
9,10-Dimethyl(1,2)benzanthracene	59	82.5	108	118	103	72.3	135	159	122	62.0	108	130	100	69.3	141	143	118
Dibenz[a,j]acridine	53	104	127	145	125	91.2	159	196	149	78.2	117	160	118	87.4	174	175	145

TABLE 15. AVERAGE RECOVERY OF POHCS FROM XAD-2 AT ≈10, 30, AND 100 µg AFTER 1-h EQUILIBRATION; HPLC/UV ANALYSIS

	Compound		
	o-Chlorophenol	Reserpine	Chlorambucil
Test Level: 10 µg			
Amount added, µg	9.39	12.0	7.03
Amount found, µg	9.66	11.4	7.35
Recovery, %	103	95.0	104
Test Level: 30 µg			
Amount added, µg	28.2	36.0	21.1
Amount found, µg	28.4	38.1	21.1
Recovery, %	101	106	100
Test Level: 100 µg			
Amount added, µg	93.9	120	70.3
Amount found, µg	98.3	116	59.4
Recovery, %	105	96.7	84.5
Average Recovery, %	103	99.2	96.2

TABLE 16. AVERAGE RECOVERY OF POHCs FROM XAD-2 AFTER LABORATORY EXPOSURE TEST; HPLC/UV ANALYSIS

Compound	Amount added, μg	Amount found, μg			Recovery, %			
		1	2	3	1	2	3	Avg
o-Chlorophenol	93.9	85.7	80.7	89.0	91.3	86.0	94.7	90.7
Reserpine	120	119	98.5	116	99.3	82.1	96.6	92.7
Chlorambucil	70.3	77.5	52.1	88.3	110	74.1	126	103

SECTION 7

GC/MS ANALYSIS OF INCINERATOR-EFFLUENT SAMPLE EXTRACTS

We applied the GC/MS analysis for POHCs to four extracts from Modified Method 5 trains (MM5) from four different incineration test sites. The samples were supplied by Midwest Research Institute and are described in Table 17. The MM5 train usually has one cartridge, but Midwest Research Institute used a multiple cartridge system. The extracts contained 20 μg/mL of decafluorobiphenyl, naphthalene-d_8, and chrysene-d_{12} as surrogate standards. At the time of GC/MS analysis, the concentrated extracts were spiked with 20 μg/mL anthracene-d_{10} as internal standards.

A summary of major POHCs that were identified and quantified in the extracts from the MM5 trains is given in Table 18. The total ion chromatograms of the extracts are presented in Figures 4 through 9.

From these extracts we were able to identify other organic compounds that are not POHCs. These compounds may be from the thermal decomposition of the sorbent material and POHCs. A summary of the major unlisted organic compounds that were identified and their retention times is given in Table 19. Because we did not analyze individual standards, we did not quantify these compounds in the MM5 extracts. Nevertheless, we have demonstrated the applicability of the generalized GC/MS analysis to samples obtained from the effluent of hazardous-waste incinerators.

TABLE 17. MODIFIED METHOD 5 TRAIN EXTRACTS FROM HAZARDOUS-WASTES-INCINERATION TRIAL BURN SITES

Extract	Description	Surrogate Added
9010-01-509-1Bl	Front XAD plus condensate	Decafluorobiphenyl Naphthalene-d_8
9025-03-138-1Bl	XAD blank	Decafluorobiphenyl Naphthalene-d_8 Chrysene-d_{12}
9025-03-503-1Bl	Front XAD plus condensate	Decafluorobiphenyl Naphthalene-d_8
9040-05-905-1Bl	2 Front XADs plus 2 back XADs plus 2 condensates	Decafluorobiphenyl Naphthalene-d_8 Chrysene-d_{12}
9042-06-504-1Bl	Front XAD plus back XAD plus condensate	Decafluorobiphenyl Naphthalene-d_8 Chrysene-d_{12}

TABLE 18. RESULTS OF ANALYSIS FOR POHCS IN EXTRACTS FROM MM5 TRAINS

Tentative identification of POHCS	Concentration of POHCs in extract, µg/mL				
	9010-01-509-1B1	9025-03-138-1B1	9025-03-503-1B1	9040-05-905-1B1	9042-06-504-1B1
Benzene	-- a	-- a	-- a	-- a	
Trichloroethene	-- a				
Trichloroethane			-- a		
Toluene	-- a	-- a		-- a	-- a
Chlorobenzene			-- a		
Dichloropropane	-- a				
Dichlorobenzene			-- a		
Bromoform			-- a		
Dichlorobenzene			-- a		
Chloronaphthalene			-- a		
Hexachlorocyclopentadiene			-- a		
Bromobenzene	2.8		99		
4-Chlorotoluene			24		
Benzaldehyde	98	27	480	1200	24
Phenol	8.0	3		300	14
2-Chlorophenol			6.9	13	
1,2,4-Trimethylbenzene	3.9	2		26	1.0
1,4-Dichlorobenzene			600	2.8	
Benzyl chloride			17		0.8
Benzyl alcohol					1.3
1,2-Dichlorobenzene			110		
N-methylaniline			12		1.3
Acetophenone	56	62	160	1900	19
4-Methylphenol				49	
Hexachloroethane			16		
Nitrobenzene			3900		
1,2,4,5-Tetramethylbenzene	1.0			6.8	0.6
4-Chlorobenzaldehyde			330	14	
Benzyl chloride			1.6		
2,4-Dimethylphenol	740				5
Nitrotoluene	12	7			
Tetralin	3.7	3	11	58	2
Propiophenone	200	20	220		120

(continued)

TABLE 18 (continued)

Tentative identification of POHCS	Concentration of POHCs in extract, µg/mL 9010-01-509-1Bl	9025-03-138-1Bl	9025-03-503-1Bl	9040-05-905-1Bl	9042-06-504-1Bl
2,6-Dimethylaniline					3
Benzoic Acid	660	6	3500	250	410
2,6-Dichlorophenol			56	1.7	
1,2,4-Trichlorobenzene			220		
Naphthlene	13	13	40	170	24
4-Chlorophenol			77	330	
4-Chloroaniline			22		
Bis(2-chloroethoxy)ethane			110		
4-Chloro-3-methylphenol				17	
4-*tert*-butylphenol				16	
4-Bromoaniline					
2-Methylnaphthalene	0.69		2.8	17	0.6
1,2,4,5-Tetrachlorobenzene			500		
2,4,6-Trichlorophenol			2300		
2,4,5-Trichlorophenol			120		
2-Chloronaphthalene				12	
Biphenyl				11	
1-Chloronaphthalene				10	
4-Methylquinoline			11		
2-Ethylnaphthalene	1.2			8	
Acenaphthylene					11
1,3-Dinitrobenzene			62		
Dimethyl phthalate	1.3				
2,4-Dinitrophenol			21		
Dibenzylfuran				4	
Pentachlorobenzene			4.7		
1-Aminonaphthalene			47		
Fluorene			3.4		0.9
4-Chloro-2-nitroaniline			11		
4-Nitroaniline				72	
Azobenzene			13		
2-Chloro-4-nitroaniline			10		
Hexachlorobenzene			2.5		
4-Aminobiphenyl			13		
Pentachlorophenol			68		
3,3'-Dichlorobiphenyl			2.6		
Pentachloronitrobenzene			9.2		
Phenanthrene	2.1		1.4	5	2

(continued)

TABLE 18(continued)

Tentative identification of POHCS	Concentration of POHCs in extract, μg/mL				
	9010-01-509-1B1	9025-03-138-1B1	9025-03-503-1B1	9040-05-905-1B1	9042-06-504-1B1
Di-*n*-butyl phthalate	23	4	22	18	29
2,4-Dinitroaniline			27		
Anthraquinone			2.9	9	
Fluoranthene	2.1				
Pyrene	1.9				
Bis(2-ethylhexyl) phthalate	14	3	71	30	16

[a] These compounds were detected but not quantified.

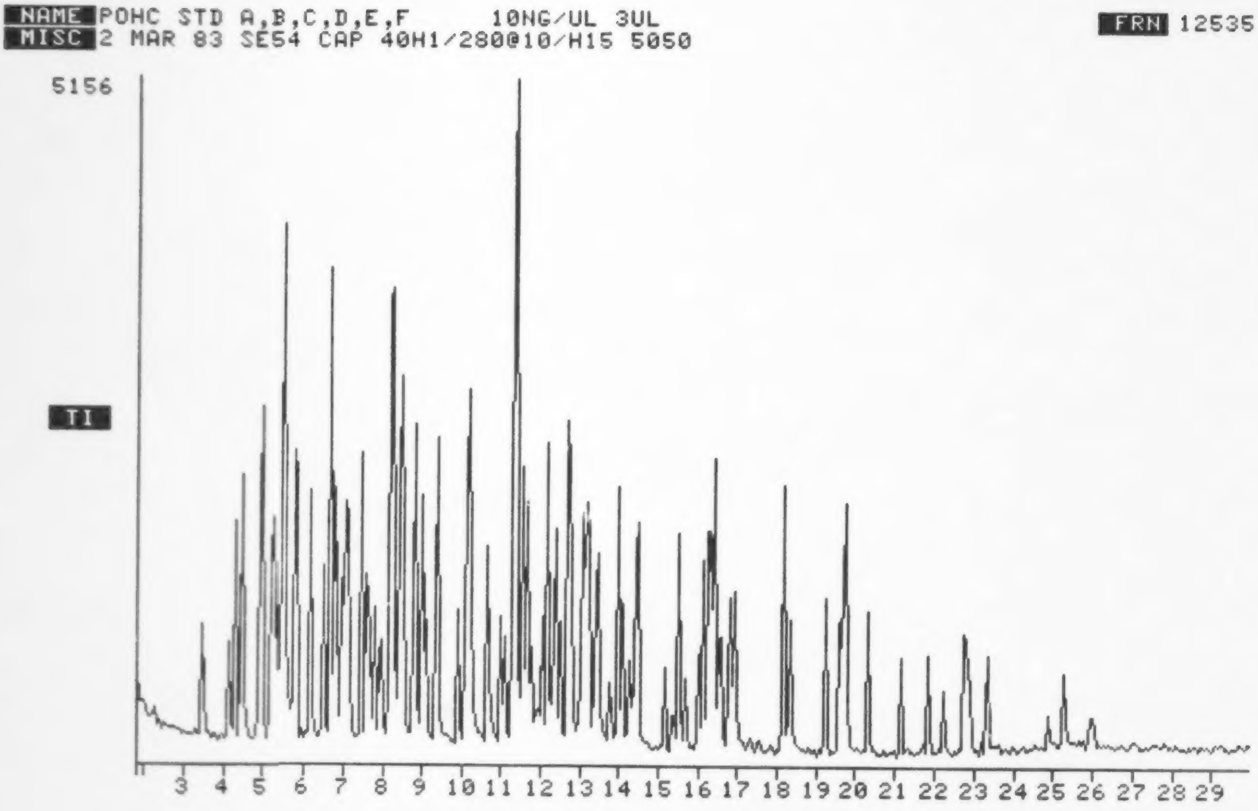


Figure 4. GC/MS chromatogram of standard POHCs mixture.

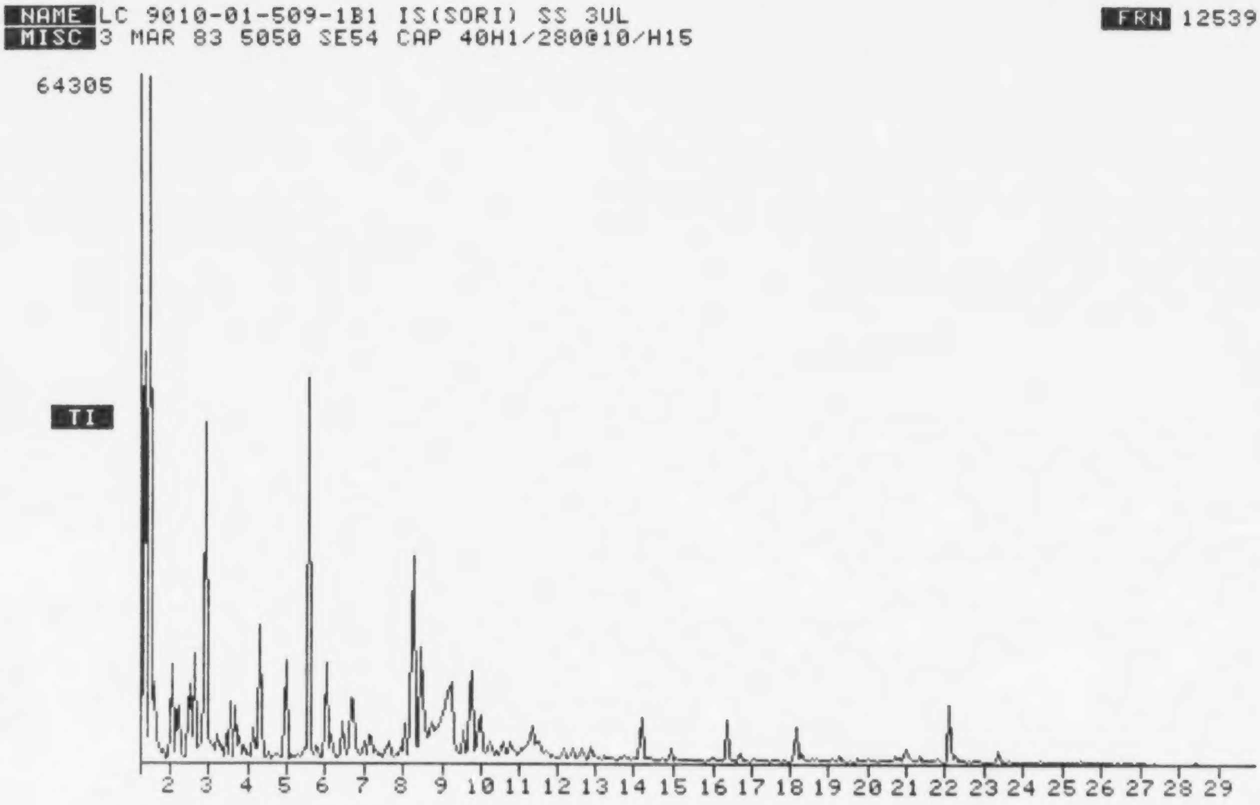


Figure 5. GC/MS chromatogram of Extract 9010-01-509-1B1.

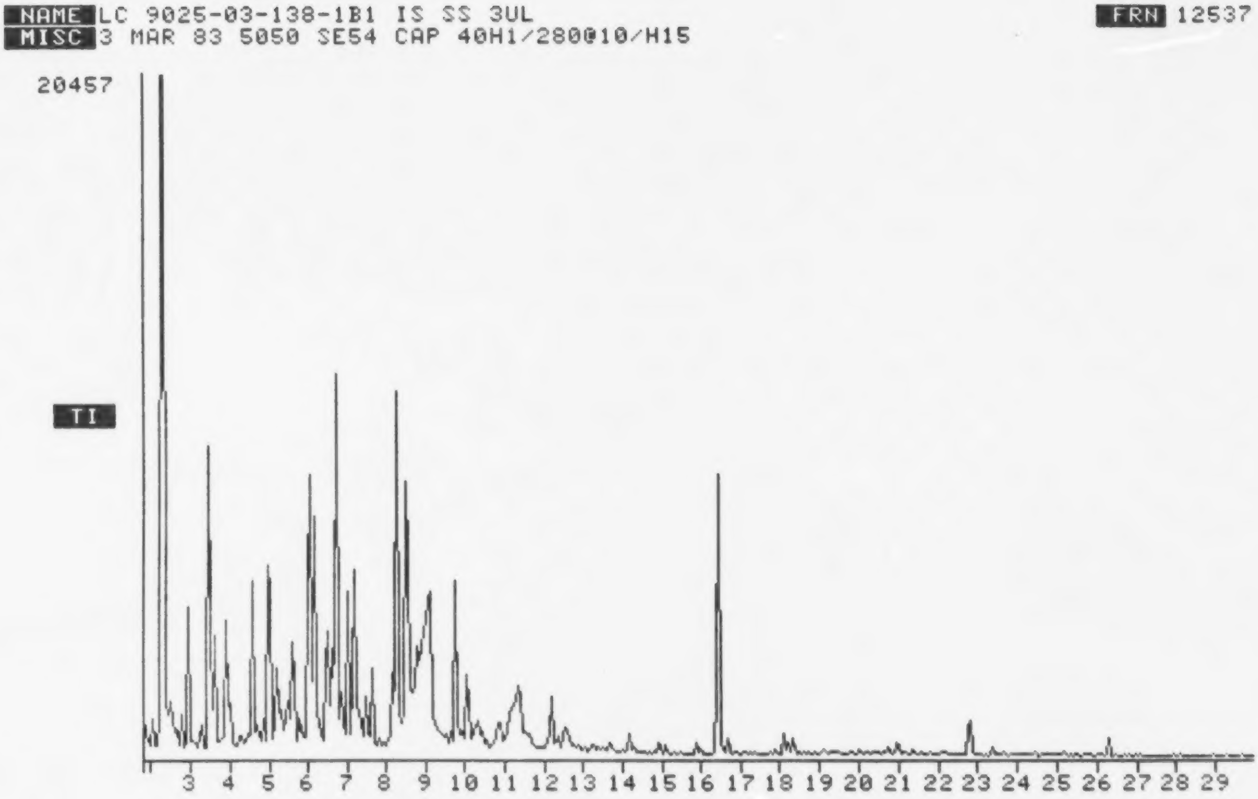


Figure 6. GC/MS chromatogram of Extract 9025-03-138-1B1.

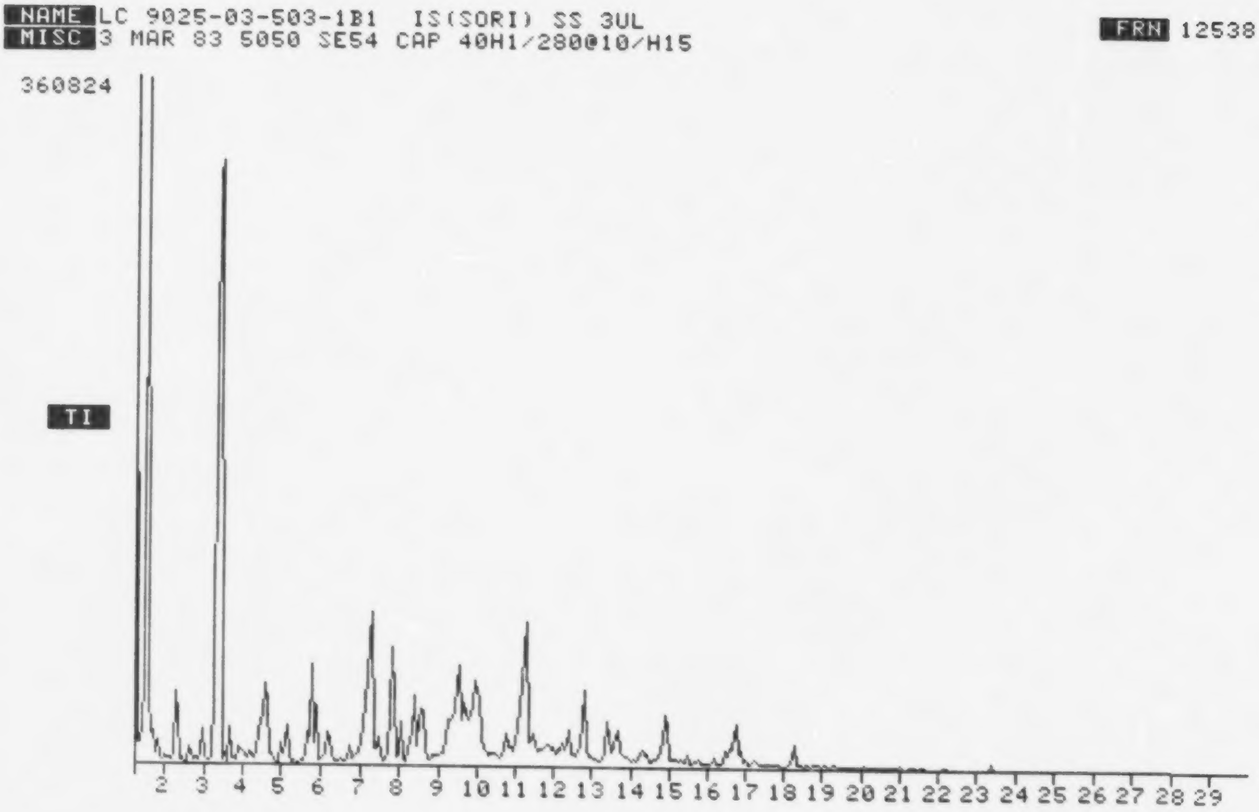


Figure 7. GC/MS chromatogram of Extract 9025-03-503-1B1.

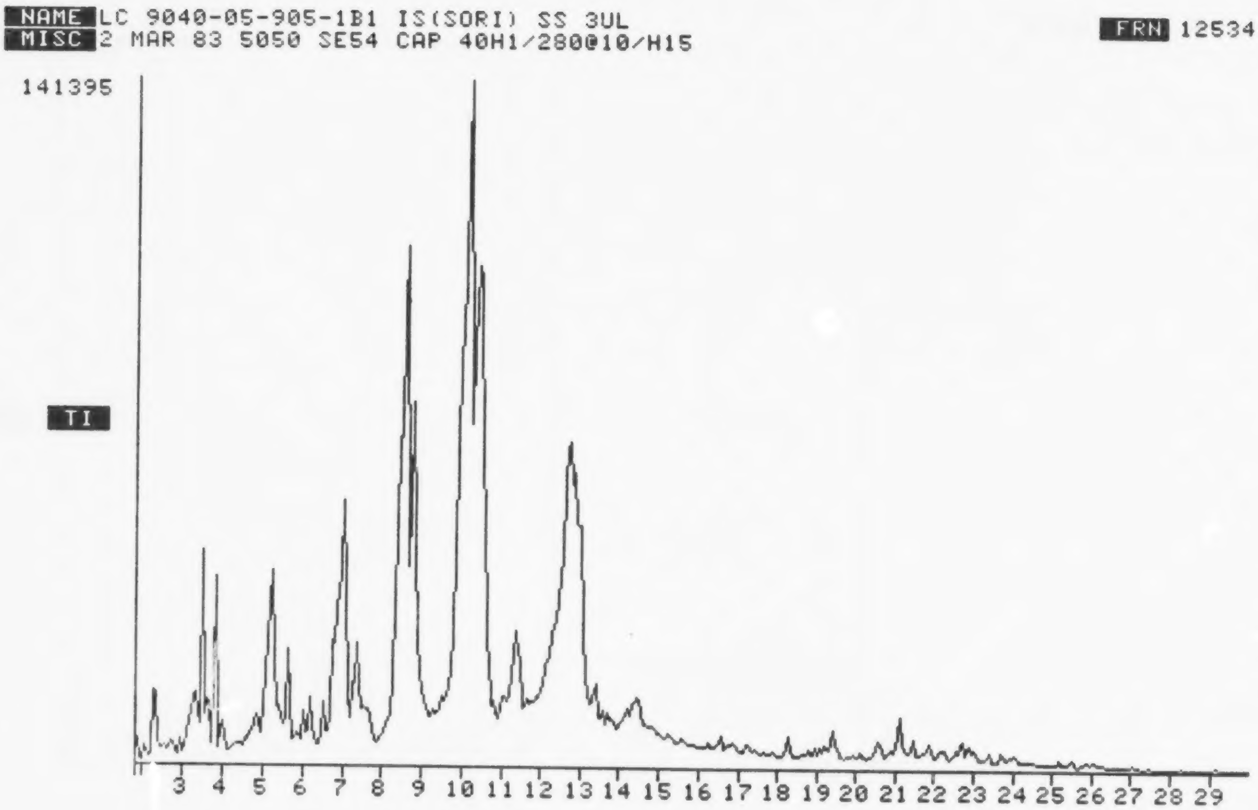


Figure 8. GC/MS chromatogram of Extract 9040-05-905-1B1.

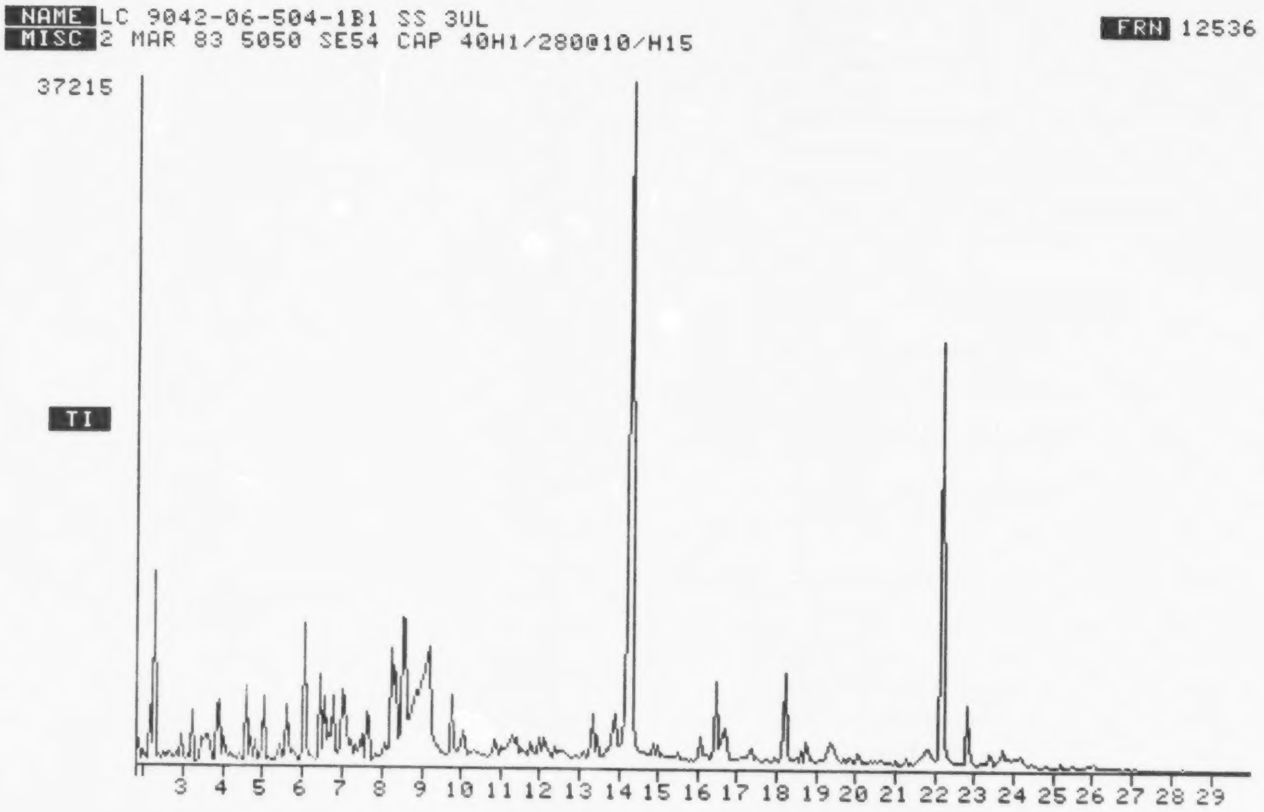


Figure 9. GC/MS chromatogram of Extract 9042-06-504-1B1.

TABLE 19. TENTATIVE IDENTIFICATION OF UNLISTED ORGANIC COMPOUNDS IN EXTRACTS FROM MM5 TRAINS

Extract	Retention time, min	Tentative identification
9010-01-509-1B1	1.5	Cyclohexane
	2.1	Unknown
	2.2	Hexenol
	2.5	Unknown
	2.7	Unknown
	2.9	Unknown
	3.6	Dimethylbenzene
	3.7	Unknown
	4.1	Unknown
	5.6	Octamethylcyclotetrasiloxane
	6.1	Unknown with chlorine
	6.5	Hydrocarbon
	8.1	Benzoic acid bis(trimethylsiloxy), Trimethylsilyl ester
	8.3	Ethylbenzaldehyde
	8.5	Methoxybenzaldehyde
	9.6	Unknown
	9.8	Dimethylacetophenone
	10.0	Unknown
	11.4	Isopropylmethylphenol
	22.2	Unknown
9025-03-138-1B1	1.5	Cyclohexane
	3.0	Unknown
	3.5	Hexenol
	2.3	Unknown
	3.5	Dimethylbenzene
	3.7	Dimethylbenzene
	3.9	Ethylenebenzene
	3.9	Cyclohexenol
	4.6	Cyclohexenone
	6.1	Hydrocarbons
	6.2	Hydrocarbons
	6.8	Trimethylbenzene

(continued)

TABLE 19 (continued)

Extract	Retention time, min	Tentative identification
9025-03-138-1B1	7.0	Methylpropenylbenzene
	7.2	Hydrocarbon
	8.3	Ethylbenzaldehyde
	8.6	Unknown
	9.8	Methylethylbenzaldehyde
	26.3	Unknown
9025-03-503-1B1	1.5	Cyclohexane
	1.9	Unknown
	2.3	Hexenol
	2.7	$CHBr_2Cl$
	3.0	Unknown with bromine
	3.7	Dimethylbenzene
	4.6	Cyclohexadienedione
	5.7	Octamethylcyclotetrasiloxane
	7.3	Chlorocyclohexadienedione
	7.5	Diethyltetrahydrofuran
	8.1	$C_6H_{10}Cl_2$ or $C_6H_{10}BrCl$
	8.4	Ethylbenzaldehyde
	8.6	Unknown with bromine
	9.5	Dichloromethylphenol
	10.1	Unknown plus benzoic acid
	10.8	Tetrachlorobenzene
	11.3	Dichloronaphthalene
	11.3	Unknown with chlorine
	12.4	Unknown with bromine
	12.8	Hydrocarbon
	13.4	Hydrocarbon
	13.6	Unknown with chlorine
	14.9	Unknown with halogens
	16.8	Unknown with halogens
	18.3	Unknown

(continued)

TABLE 19 (continued)

Extract	Retention time, min	Tentative identification
9040-05-905-1B1	1.6	Cyclohexane
	2.1	Butenoic acid, methyl ester
	3.3	Dimethylfuran
	3.6	Dimethylbenzene
	3.7	Dimethylbenzene
	3.9	Octamethyltrisiloxane
	5.7	Octamethylcyclotetrasiloxane
	7.1	Ethylstyrene
	8.5	*tert*-Butylbenzene
	8.5	Terephthaldehyde
	8.6	Dimethylphenol
	8.8	Cinnamaldehyde
	10.2	Dimethylacetophenone
	10.4	Unknown
	12.7	Diisopropylbenzene
	19.5	Unknown
	21.2	Methyl-*tert*-butylbenzene
	21.5	Methyl-*tert*-butylbenzene
9042-06-504-1B1	1.5	Cyclohexane
	1.8	Unknown
	2.2	Unknown
	3.2	Unknown
	3.9	Ethenylbenzene
	4.6	Cyclohexenone
	5.6	Octamethylcyclotetrasiloxane
	6.1	Unknown
	6.5	Diethylbenzene
	6.8	Hydrocarbon
	7.1	Dimethylethenylbenzene
	8.3	Prophenylphenol
	8.6	Methyl benzoate
	9.8	Ethyltrimethylbenzene
	13.4	Unknown
	14.3	Phthalate
	21.8	Unknown
	22.2	Unknown

SECTION 8

QUALITY-ASSURANCE SUMMARY

The work that was done at SoRI and presented in this report was performed under SoRI Quality Assurance plan for Contract 68-02-3696, Work Assignment 001, July 1982. Although the project includes environmentally related measurement activities, SoRI was not involved in field sampling or the preparation of field samples for analysis. Thus, sampling procedures, chain-of-custody procedures, and spiked sample matrixes were considered as nonapplicable in the systematic review of this project. The major efforts of SoRI were to evaluate and, when necessary, modify GC/MS and HPLC/UV generalized analysis procedures for approximately 100 candidate POHCs. This task was accomplished with individual POHCs and mixtures of POHCs.

An internal audit of the project revealed no deficiencies in the internal quality-control checks and data processing. The relative retention times, on-column detection limits, chromatograms, calibration curves, relative ion abundances, mass spectra, and relative standard deviations in this report will be a guide for other analytical laboratories. Because of subtle differences among laboratories and analytical instrumentation, analysts who participate in similar studies should generate data that will establish their own criteria for the analysis of POHCs.

SECTION 9

PROJECT SUMMARY

EPA compiled a manual entitled "Sampling and Analysis Methods for Hazardous Waste Combustion," February 1984, which is intended to be a resource document for the preparation and execution of a sampling and analysis plan for hazardous-waste incinerators. The Methods Manual recommends a variety of analytical techniques for the determination of POHCs. Methods were written to incorporate fused-silica capillary gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC). These methods were designed to provide satisfactory qualitative and quantitative analyses on a cost-effective basis for a variety of waste types and process chemistries. Generalized GC/MS and HPLC techniques were developed for the determination of as many of the POHCs as possible.

We structured our laboratory work to lead systematically from the determination of the feasibility of developing generalized test methods to the standardization of the resulting methods for selected POHCs. Initially, we performed analyses of standard solutions of mixtures of selected POHCs to optimize instrumental operating conditions. Then we obtained individual chromatograms (GC/FID, GC/MS, and HPLC/UV), established calibration curves, and estimated limits of detection. The technical approach in the development and evaluation of the generalized instrumental methods is discussed in this report. The chromatograms and data are provided in three appendixes of this report.

Appendix A contains the chromatograms and calibration curves for the GC/FID determinations. Appendix B shows the mass spectra in addition to the chromatograms and calibration curves for GC/MS determinations. Appendix C contains the UV absorption spectra as well as the chromatograms and calibration curves for HPLC/UV determinations.

The sampling methods required for the determination of POHCs in hazardous wastes and incinerator effluents during trial burns will vary according to the nature of the wastes. Prior to incineration, the hazardous waste may be a solid, liquid, slurry, or sludge. After incineration, the POHCs may be found in bottom ash, fly ash/ESP catches, scrubber water, or stack gas.

During trial burns, the measurement of POHCs in the stack-gas effluent is necessary for the calculation of DRE values to determine if the incinerator meets its performance criteria. The sampling of stack-gas components is most important to the process of obtaining permits for hazardous-waste incinerators. Some of the sampling methods available to collect volatile POHCs at low concentrations in stack gas are the Modified Method 5 (MM5) sampling train, the Source Assessment Sampling System (SASS), and the Volatile Organic Sampling Train (VOST). These systems use specific sorbents to collect POHCs. We selected XAD-2 resin, a general-purpose sorbent for organic compounds, to determine its adsorption of and, subsequently, the recovery of POHCs.

In this preliminary study, 25 POHCs, 13 internal standards, and 3 surrogate standards were determined by GC/MS. An additional 7 POHCs were determined by HPLC/UV.

We do not intend to make conclusions based solely on the result of this one study, but certain trends were observed. The test results may be influenced by the method used to quantitate the data.

The average recovery of POHCs from the sorbent was determined by GC/MS using an internal standard method (phenanthrene-d_{10} added prior to GC/MS analysis) and by surrogate standards spiked in the sorbent tubes along with the POHCs. For sorbent tubes spiked at a 100-μg level and equilibrated for 1 h, the average percent recovery was 110% based on internal standard and 79% based on surrogate standards. The average percent recovery of the 100-μg level equilibrated for 72 h was 103% based on internal standard and 76% based on surrogate standards. If the POHCs were determined by HPLC/UV, then the average percent recovery was 99% for ≈10-, 30-, and 100-μg levels after 1-h equilibration.

Also we have applied the generalized GC/MS analysis to four extracts from Modified Method 5 trains from four different incineration test sites. We were able to detect some POHCs and other compounds that may be from the thermal decomposition of the sorbent material.

We believe that these data are encouraging. They should be the foundation for the design of more comprehensive studies of sampling, sample preparation, and sample analysis in support of the program for incineration of hazardous waste.

REFERENCES

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3. Vogel, G.; Brooks, K.; Cross, J.; Frankel, I.; Haus, S.; and Jacobsen, W. Guidance manual for evaluating permit applications for the operation of hazardous waste incinerator units. Final Report, EPA Contract 68-01-6092, U.S. Environmental Protection Agency, Washington, D.C.; 1981 April.

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5. de Vera, E.R.; Simmons, B.P.; Stephens, R.D.; Storm, D.L. Samplers and sampling procedures for hazardous waste streams. EPA-600/2-80-018, NTIS PB 80-135-353, U.S. Environmental Protection Agency, Cincinnati, OH; 1980.

APPENDIX A

CHROMATOGRAMS AND CALIBRATION CURVES FOR GC/FID DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference calibration curve Figure No.
Acetophenone	A-1	A-2
4-Aminobiphenyl	A-1	A-4
Aniline	A-6	A-7
Aramite	A-44	A-46
Benzenethiol	A-10	--
Butylbenzyl phthalate	A-31	A-35
Chlorobenzilate	A-47	A-51
p-Chloro-*m*-cresol	A-19	A-21
2-Chlorophenol	A-13	A-14
3-Chloropropionitrile	A-61	A-63
m-Cresol	A-52	A-55
o-Cresol	A-19	A-20
p-Cresol	A-47	A-49
Diallate	A-24	A-25
Dibutyl phthalate	A-19	A-23
(Dichloromethyl)benzene	A-56	A-58
Diethyl phthalate	A-31	A-33
Diisobutyl phthalate	A-31	A-34
Dimethoate	A-47	A-50
p-Dimethylaminoazobenzene	A-6	A-9
α,α-Dimethylphenethylamine	A-61	A-64
2,4-Dimethylphenol	A-27	A-28
Dimethyl phthalate	A-31	A-32
4,6-Dinitro-*o*-cresol	A-19	A-22
Dioctyl phthalate	A-31	A-36
Diphenylamine	A-37	A-38
Disulfoton	A-24	A-26
Ethyl carbamate	A-39	A-40
Ethyl methacrylate	A-52	A-54
Hexachlorophene	A-27	A-30
Isosafrole	A-44	A-45
Kepone	A-1	A-5
Methoxychlor	A-13	A-18

(continued)

APPENDIX A

CHROMATOGRAMS, AND CALIBRATION CURVES FOR GC/FID DETERMINATIONS

Index

(continued)

Compound	Reference chromatogram Figure No.	Reference calibration curve Figure No.
4,4'-Methylenebis(2-chloroaniline)	A-61	A-65
2-Methyllactonitrile	A-47	A-48
Methyl methacrylate	A-52	A-53
Methyl methanesulfonate	A-56	A-57
Methyl parathion	A-10	A-12
2-Naphthylamine	A-39	A-43
Octamethyl pyrophosphoramide	A-10	A-11
Pentachloronitrobenzene	A-13	A-17
Pentachlorophenol	A-13	A-16
m-Phenylenediamine	A-39	A-42
o-Phenylenediamine	A-39	A-41
p-Phenylenediamine	A-1	A-3
Phosphorodithioic acid ester[a]	A-56	A-59
Phosphorothioic acid ester[b]	A-56	A-60
Pyridine	A-61	A-62
2,3,4,6-Tetrachlorophenol	A-13	A-15
2,4,6-Trichlorophenol	A-27	A-29
O,*O*,*O*-triethyl phosphorothioate	A-6	A-8

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[a] Phosphorodithioic acid, *O*,*O*-diethyl *S*-((ethylthio)methyl) ester.

[b] Phosphorothioic acid, *O*,*O*-dimethyl *O*-(*p*-((dimethylamino)sulfonyl) phenyl) ester.

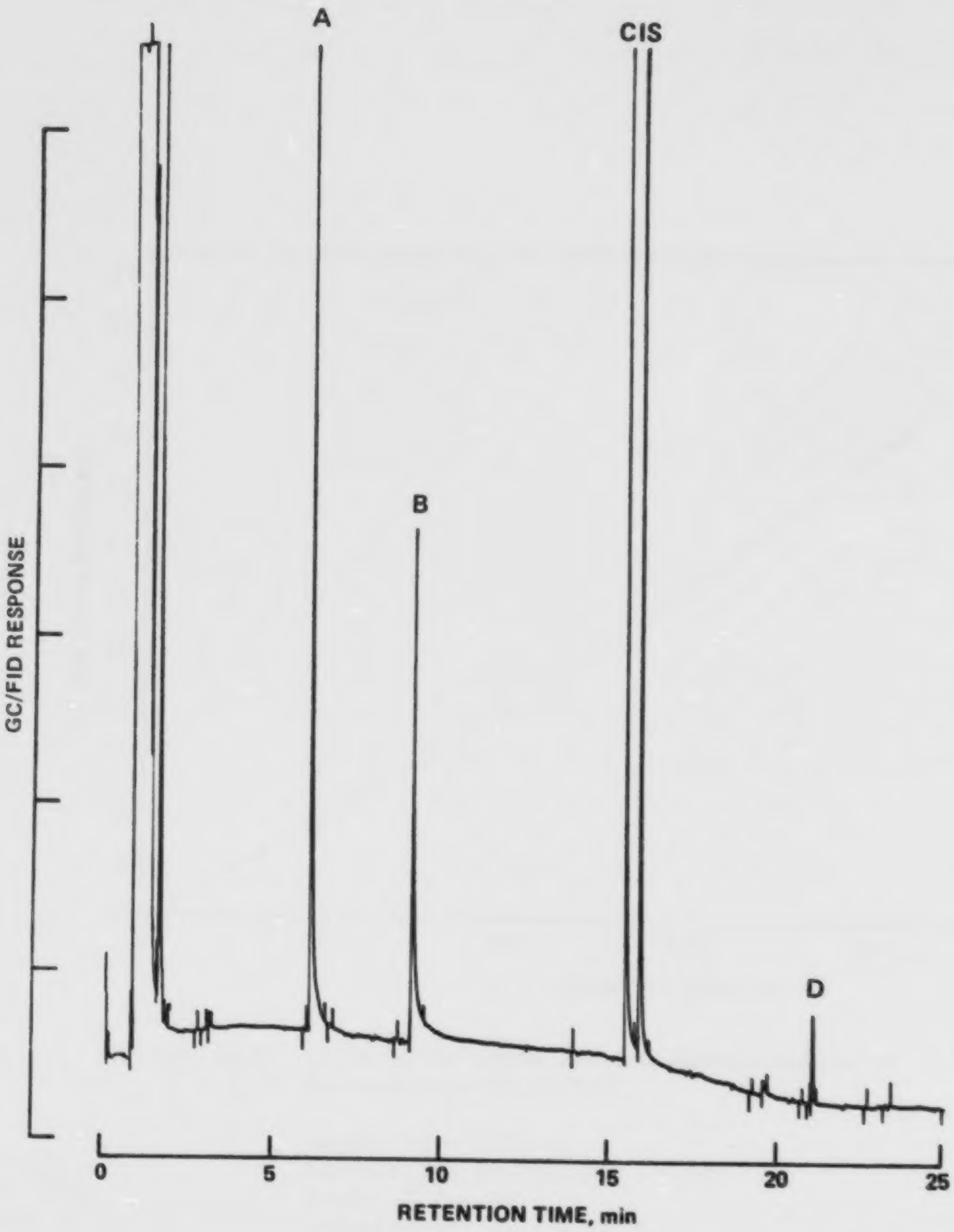

Figure A-1. Chromatogram by GC/FID for

(A) acetophenone(t_R = 6.1 min),
(B) p-phenylenediamine(t_R = 9.2 min),
(C) 4-aminobiphenyl(t_R = 15.5 min), and
(D) kepone(t_R = 21.0 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

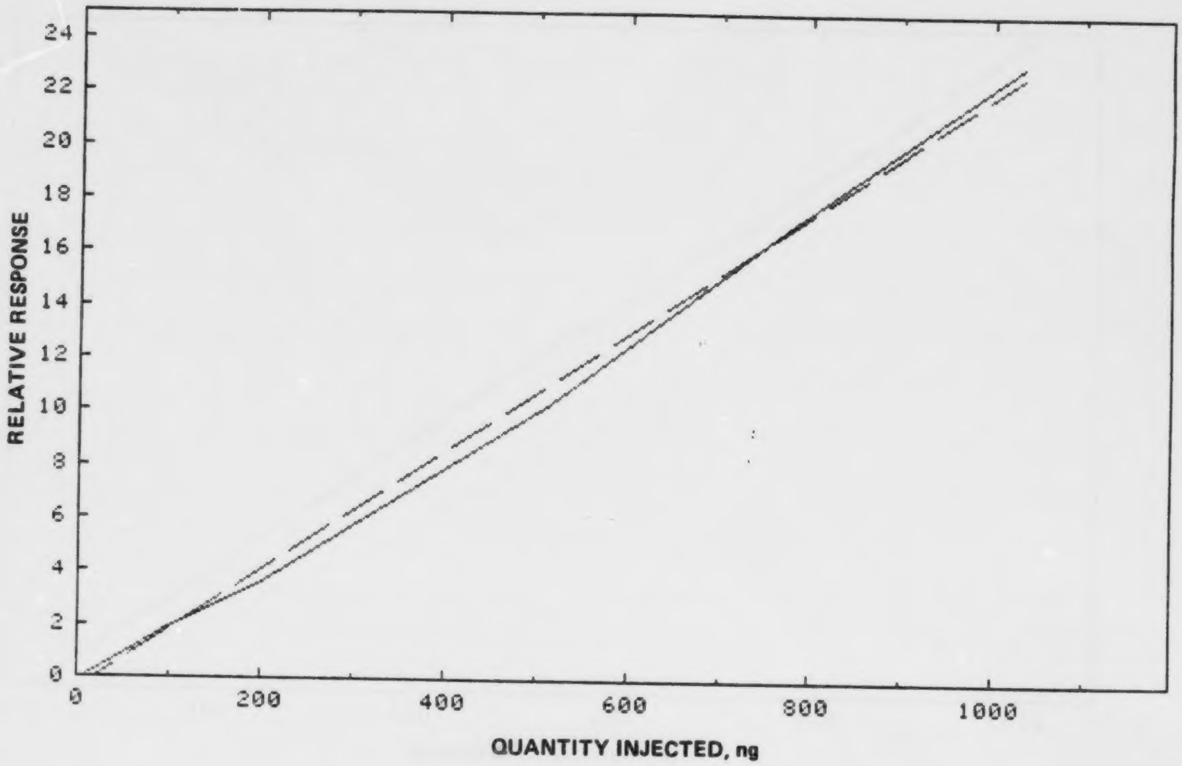

Figure A-2. Calibration curve for the determination of acetophenone by GC/FID.

Range: 52 - 1000 ng
Correlation coefficient: 0.999
Slope: 2.2×10^{-2}
y-Intercept: -4.3×10^{-1}

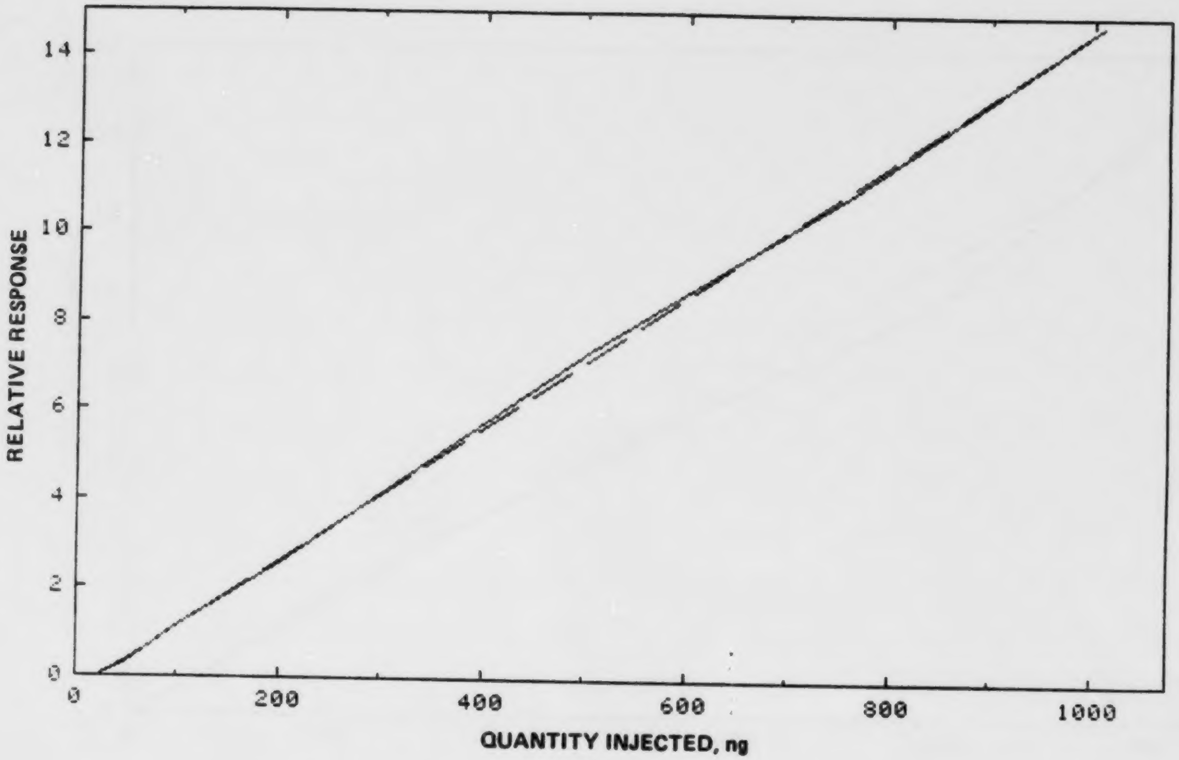

Figure A-3. Calibration curve for the determination of *p*-phenylenediamine by GC/FID.

Range: 50 - 1000 ng
Correlation coefficient: 0.999
Slope: 1.5×10^{-2}
y-Intercept: -3.5×10^{-1}

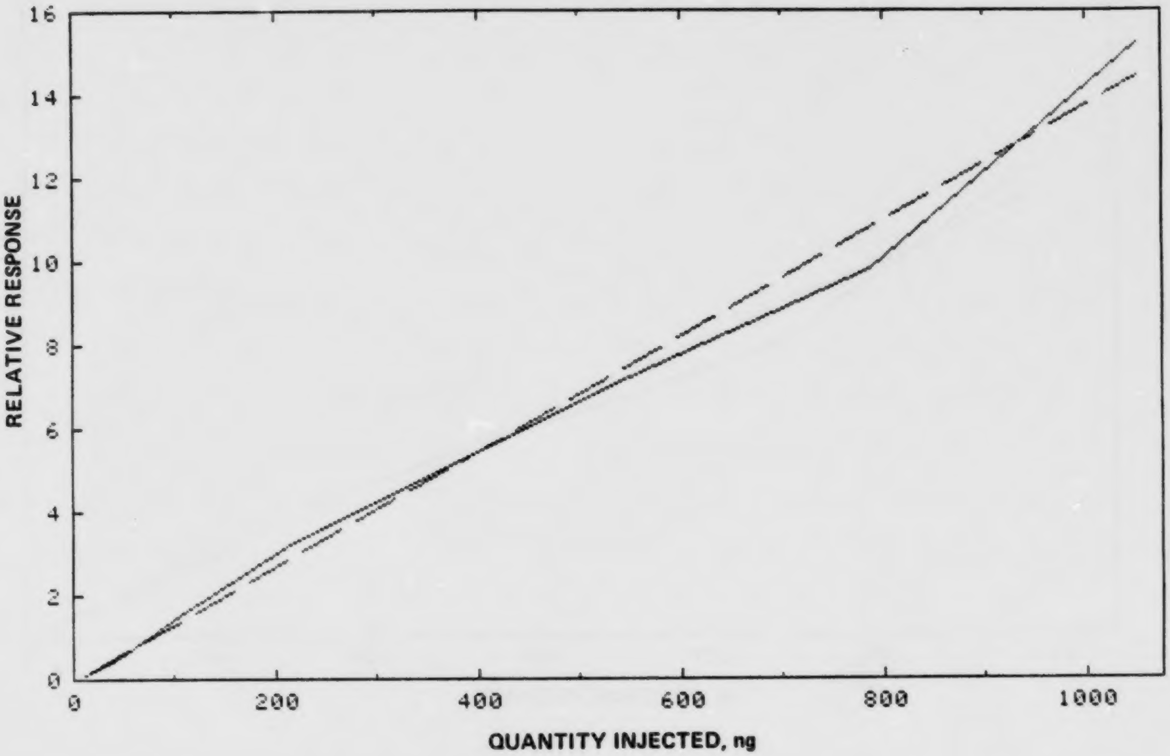

Figure A-4. Calibration curve for the determination of 4-aminobiphenyl by GC/FID.

Range: 10 - 1000 ng
Correlation coefficient: 0.996
Slope: 1.4×10^{-2}
y-Intercept: -6.5×10^{-2}

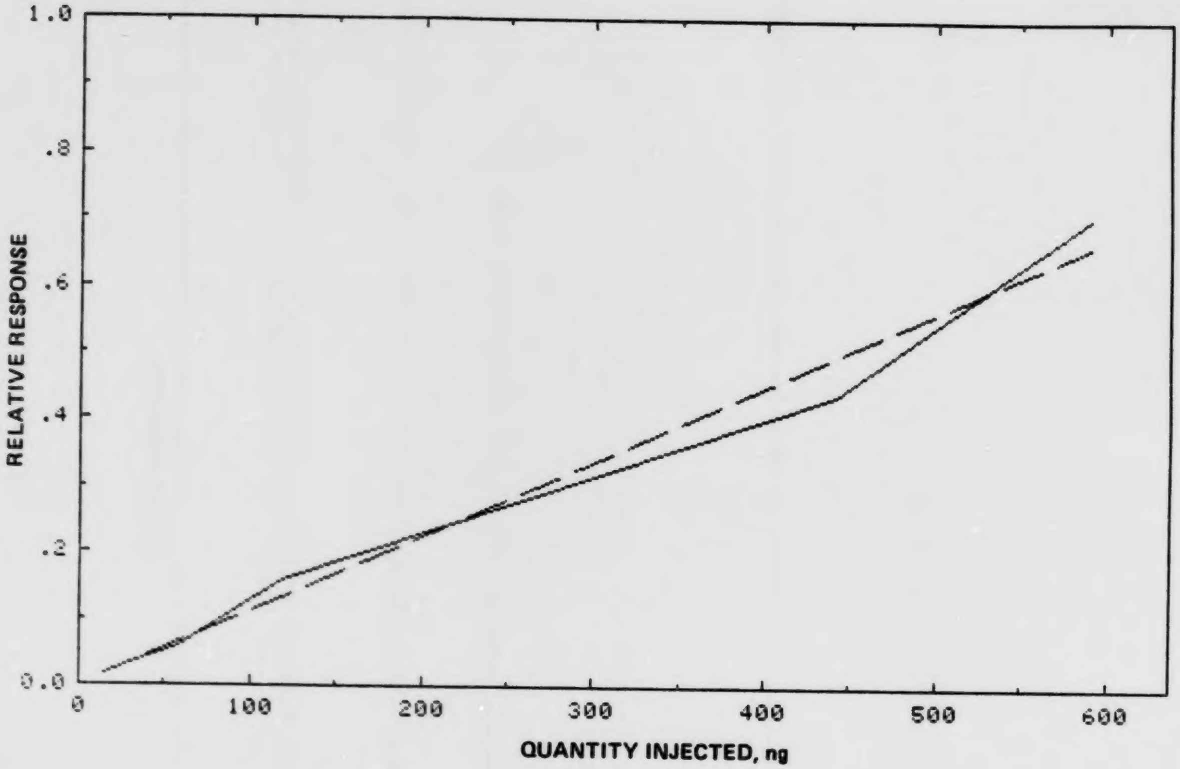

Figure A-5. Calibration curve for the determination of kepone by GC/FID.

Range: 15 - 590 ng
Correlation coefficient: 0.992
Slope: 1.1×10^{-3}
y-Intercept: 4.0×10^{-4}

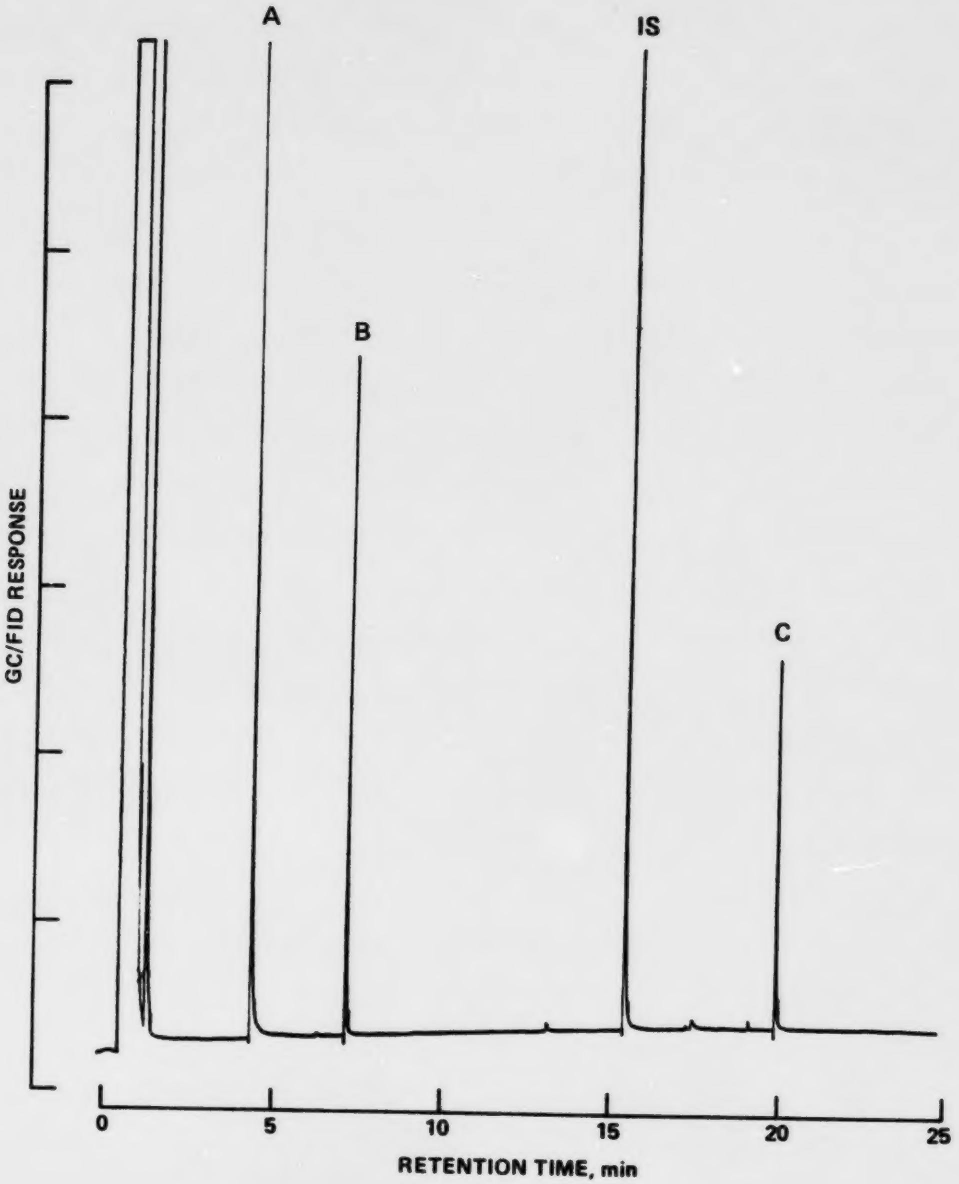

Figure A-6. Chromatogram by GC/FID for

(A) aniline(t_R = 4.7 min),
(B) O,O,O-triethyl phosphorothioate(t_R = 7.6 min), and
(C) p-dimethylaminoazobenzene(t_R = 20.3 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

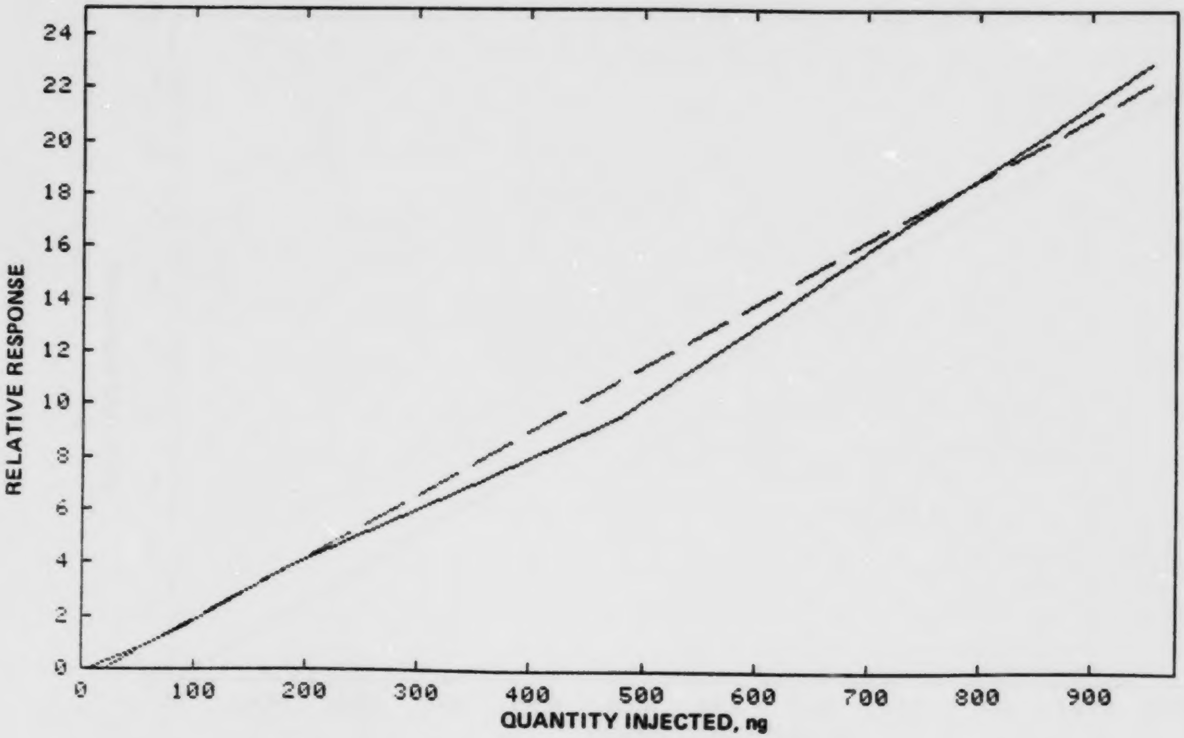

Figure A-7. Calibration curve for the determination of aniline by GC/FID.

Range: 48 - 950 ng
Correlation coefficient: 0.991
Slope: 2.6 x 10^{-2}
y-Intercept: -5.6 x 10^{-1}

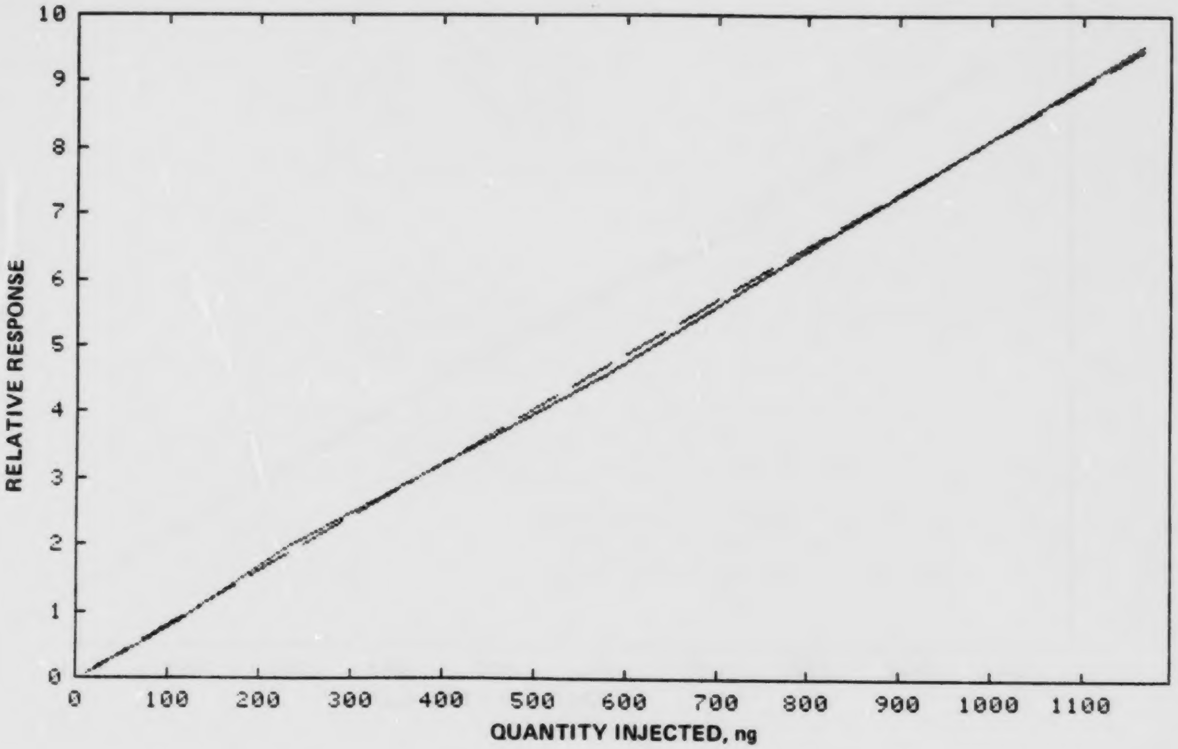

Figure A-8. Calibration curve for the determination of O,O,O-triethyl phosphorothioate by GC/FID.

Range: 12 - 1200 ng
Correlation coefficient: 0.994
Slope: 8.6×10^{-3}
y-Intercept: -4.8×10^{-2}

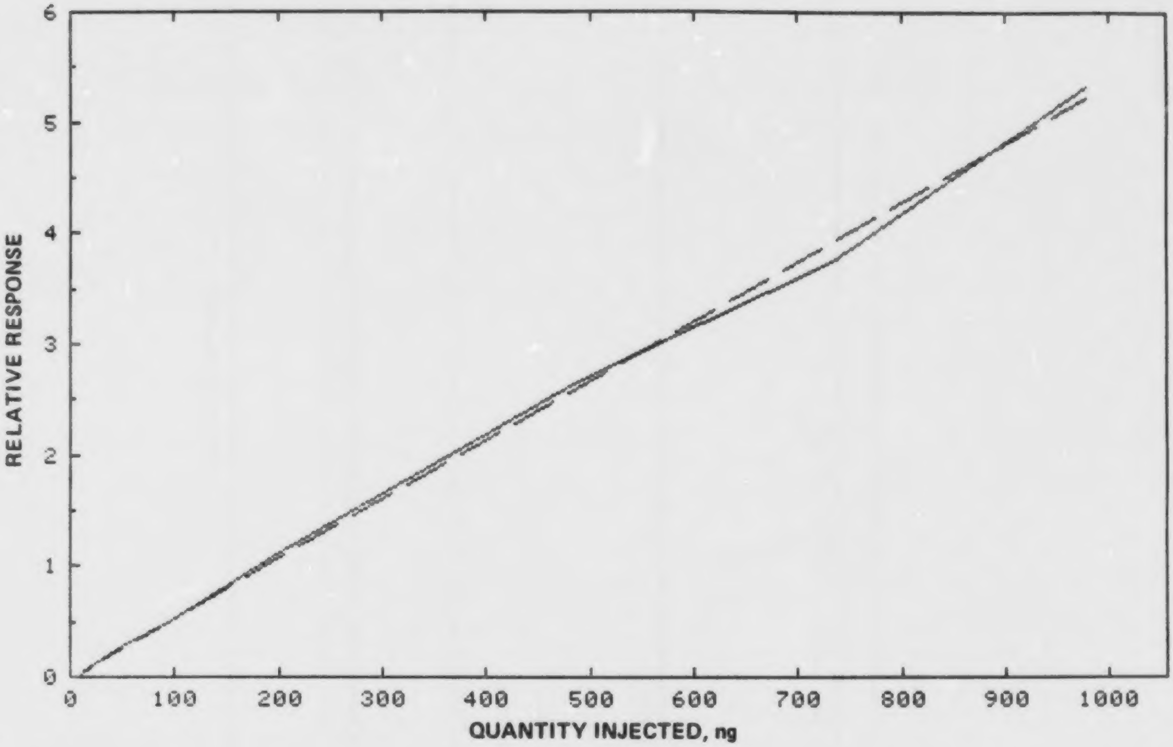

Figure A-9. Calibration curve for the determination of p-dimethylaminoazobenzene by GC/FID.

Range: 24 - 980 ng
Correlation coefficient: 0.999
Slope: 5.4×10^{-3}
y-Intercept: -4.5×10^{-3}

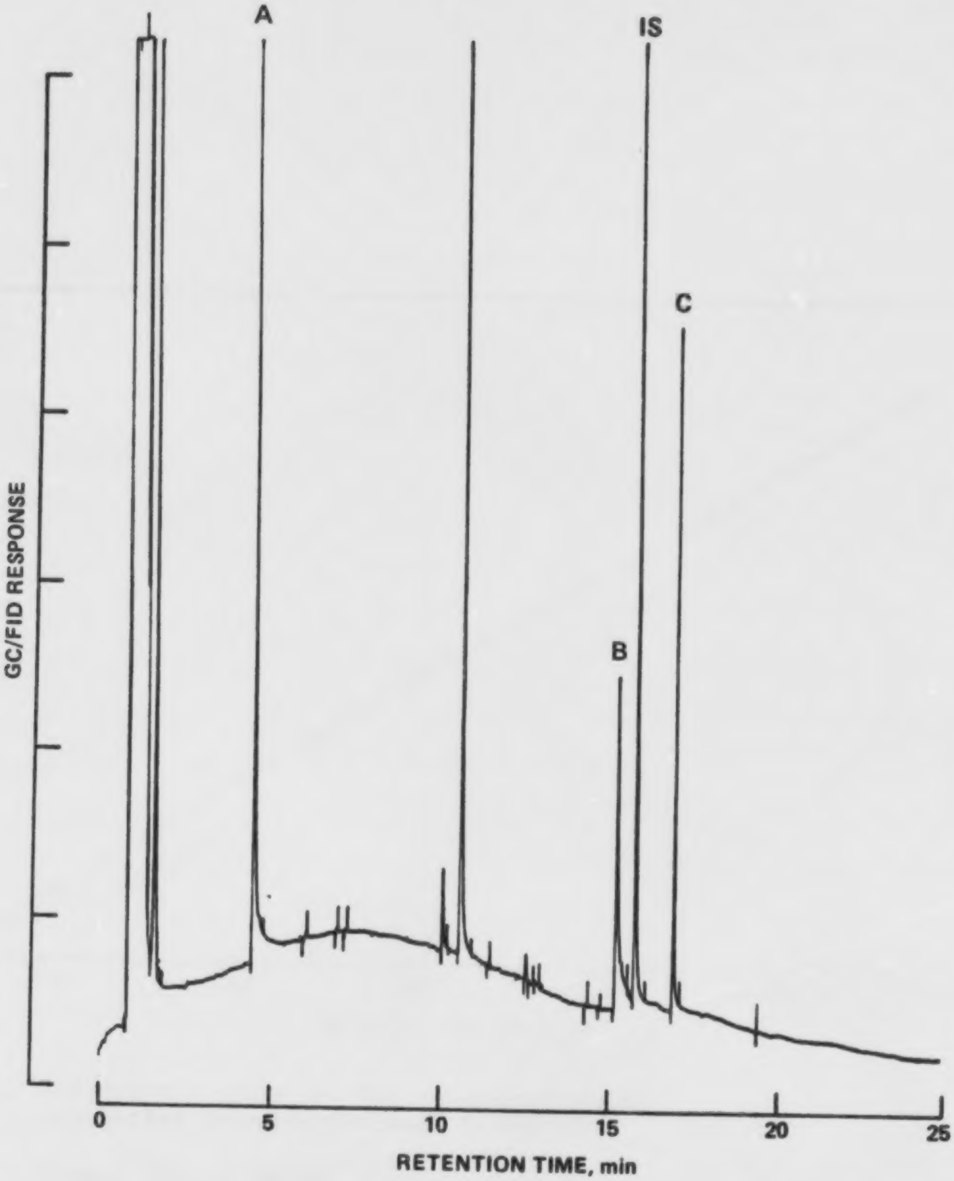

Figure A-10. Chromatogram by GC/FID for

(A) benzenethiol(t_R = 4.5 min),
(B) octamethyl pyrophosphoramide(t_R = 15.4 min) and
(C) methyl parathion(t_R = 17.1 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

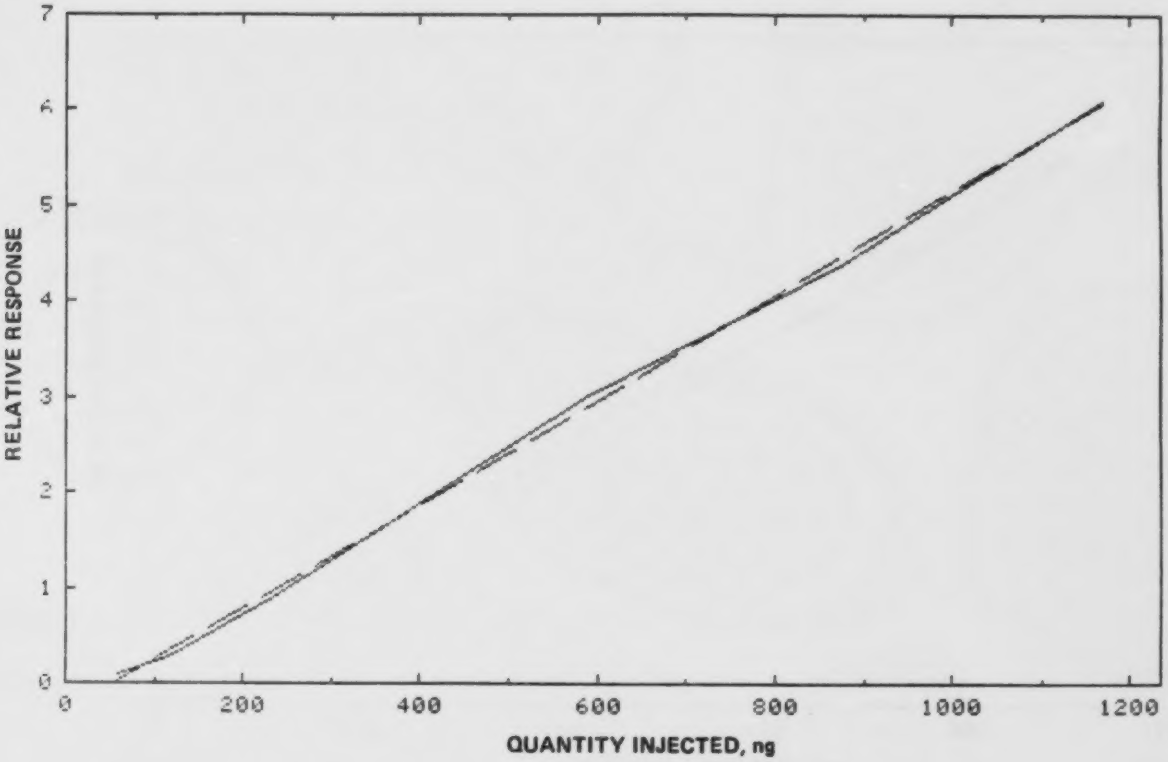

Figure A-11. Calibration curve for the determination of octamethyl pyrophosphoramide by GC/FID.

Range: 120 - 1200 ng
Correlation coefficient: 0.999
Slope: 5.4×10^{-3}
y-Intercept: -3.0×10^{-1}

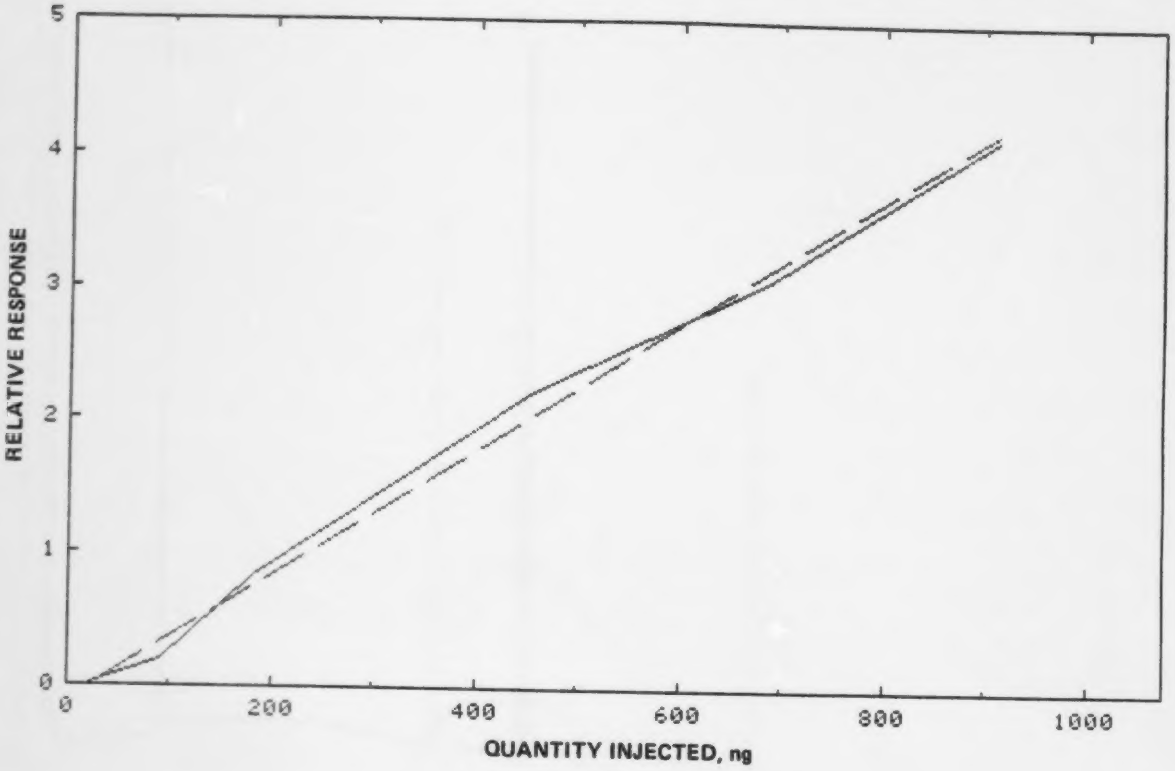

Figure A-12. Calibration curve for the determination of methyl parathion by GC/FID.

Range: 91 - 910 ng
Correlation coefficient: 0.998
Slope: 4.7×10^{-3}
y-Intercept: -1.0×10^{-1}

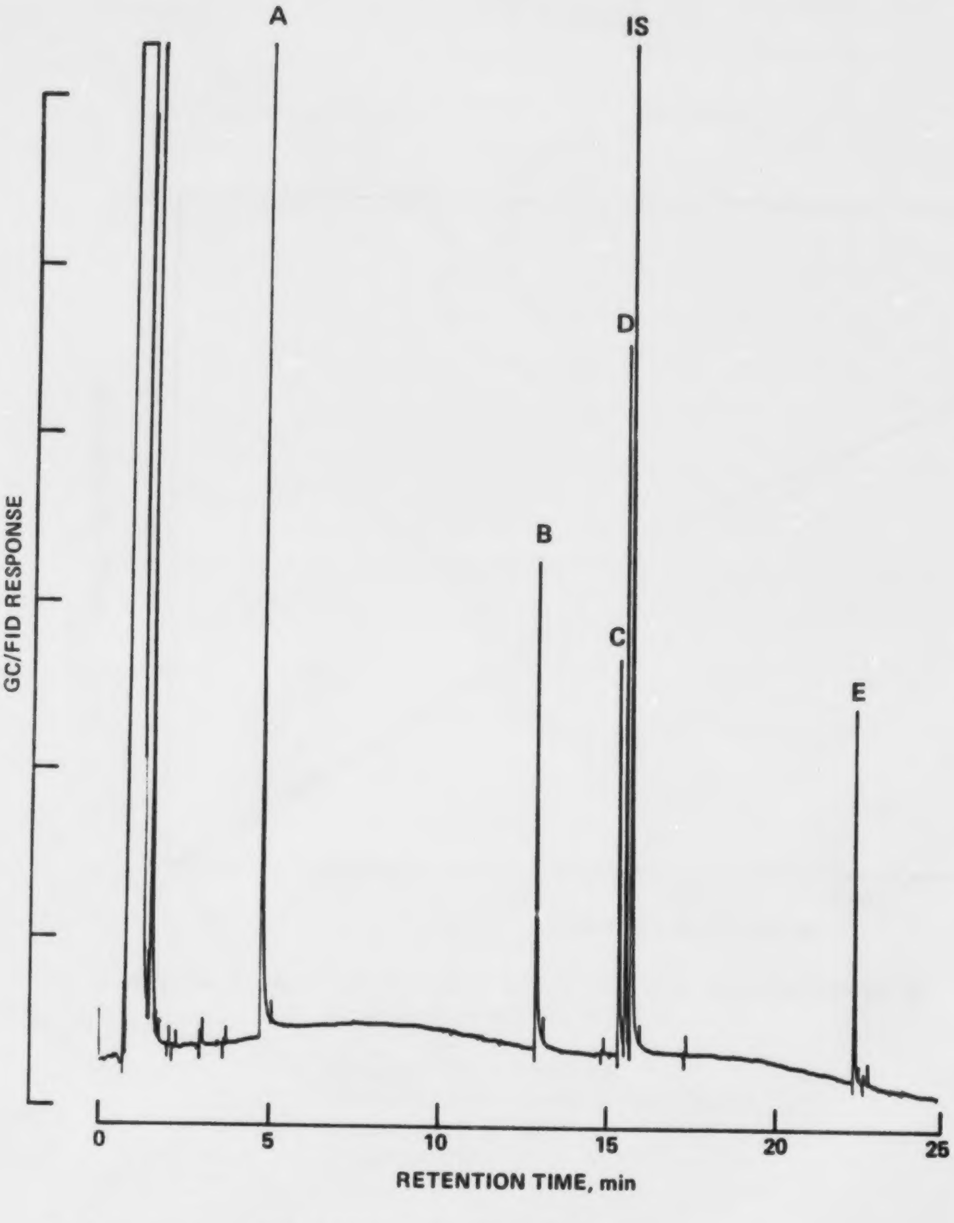

Figure A-13. Chromatogram by GC/FID for

(A) 2-chlorophenol(t_R = 4.9 min),
(B) 2,3,4,6-tetrachlorophenol(t_R = 13.1 min),
(C) pentachlorophenol(t_R = 15.6 min),
(D) pentachloronitrobenzene(t_R = 15.8 min), and
(E) methoxychlor(t_R = 22.6 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °, 15 min isothermal

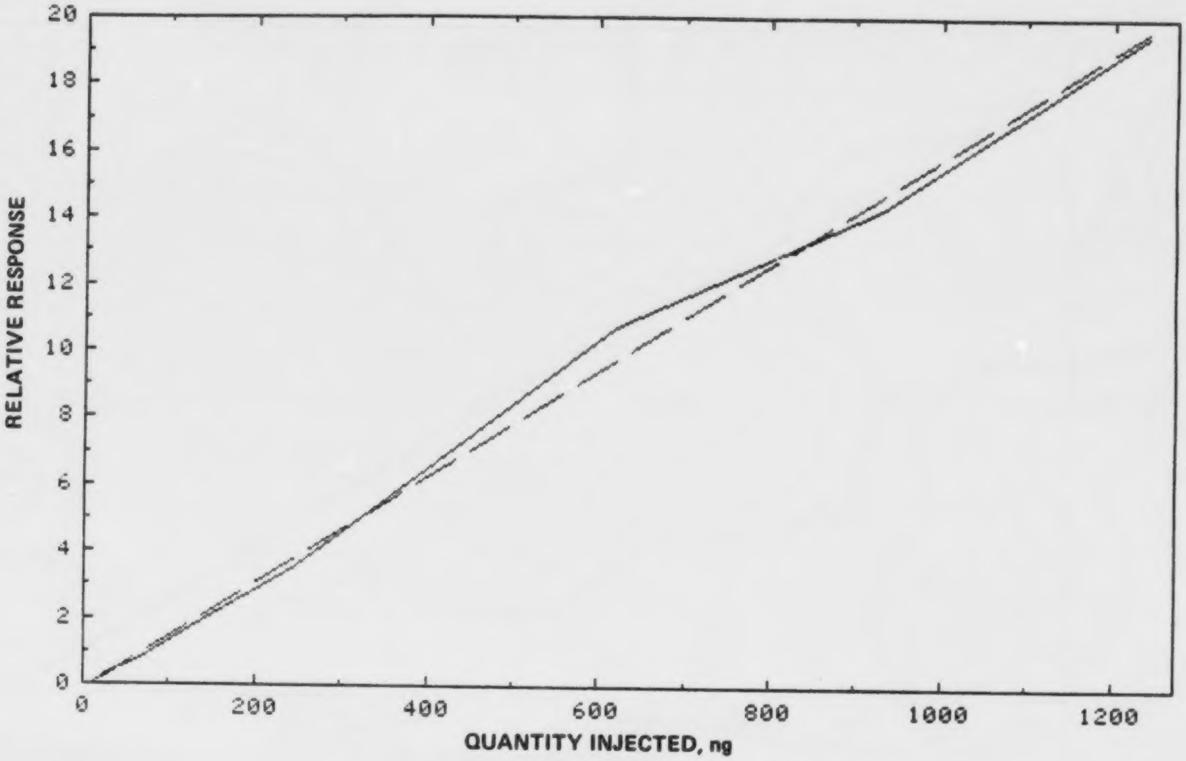

Figure A-14. Calibration curve for the determination of 2-chlorophenol by GC/FID.

Range: 31 - 1200 ng
Correlation coefficient: 0.998
Slope: 1.6×10^{-2}
y-Intercept: -1.5×10^{-1}

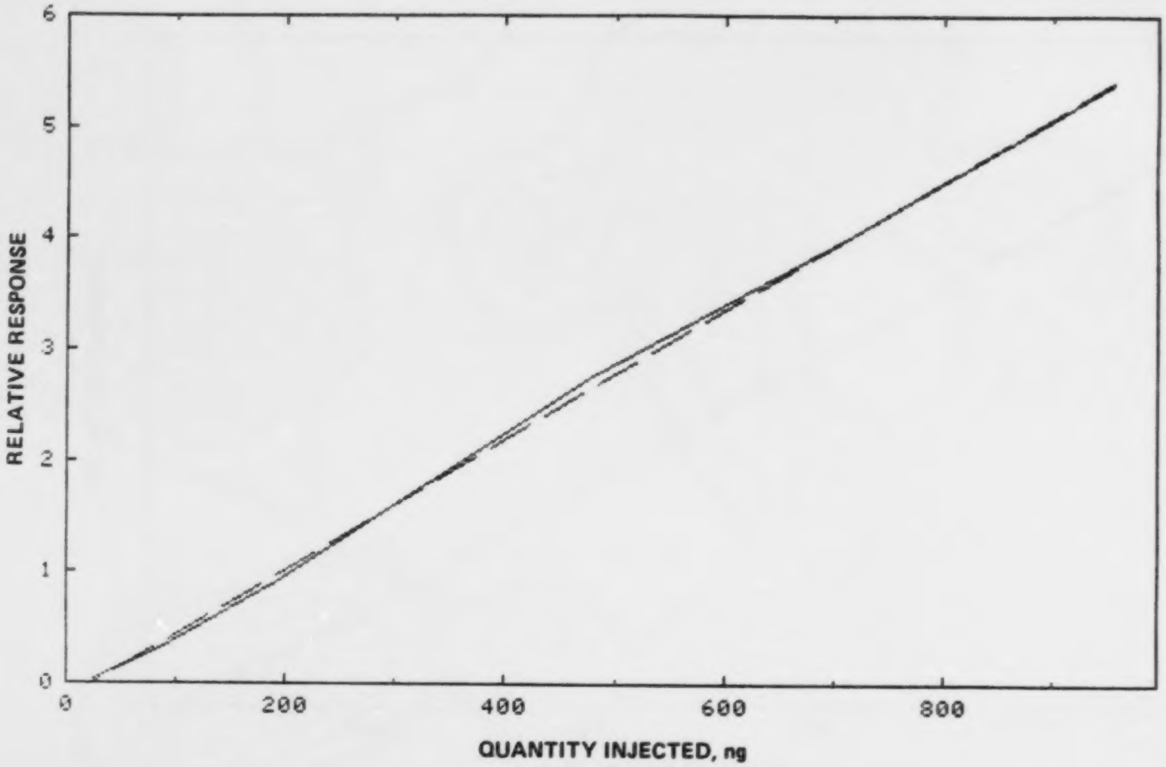

Figure A-15. Calibration curve for the determination of 2,3,4,6-tetrachlorophenol by GC/FID.

Range: 48 - 950 ng
Correlation coefficient: 0.999
Slope: 5.8×10^{-3}
y-Intercept: -1.4×10^{-1}

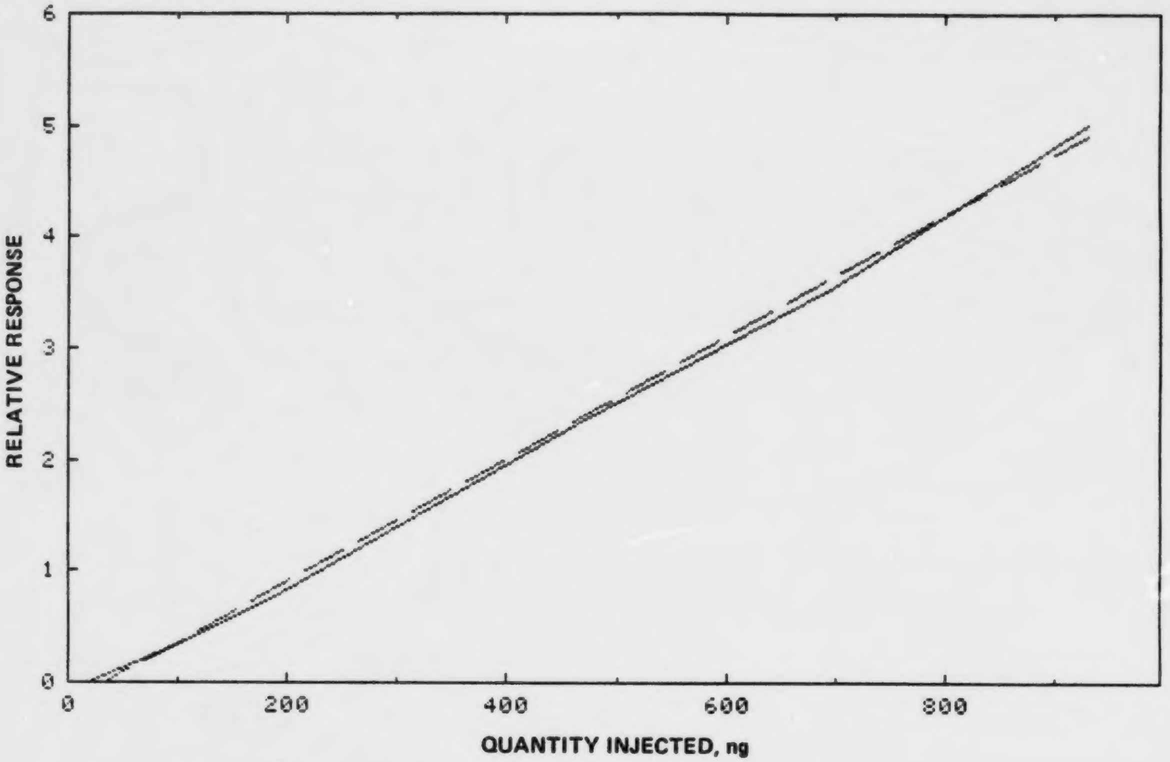

Figure A-16. Calibration curve for the determination of pentachlorophenol by GC/FID.

Range: 93 - 930 ng
Correlation coefficient: 0.999
Slope: 5.5×10^{-3}
y-Intercept: -1.8×10^{-1}

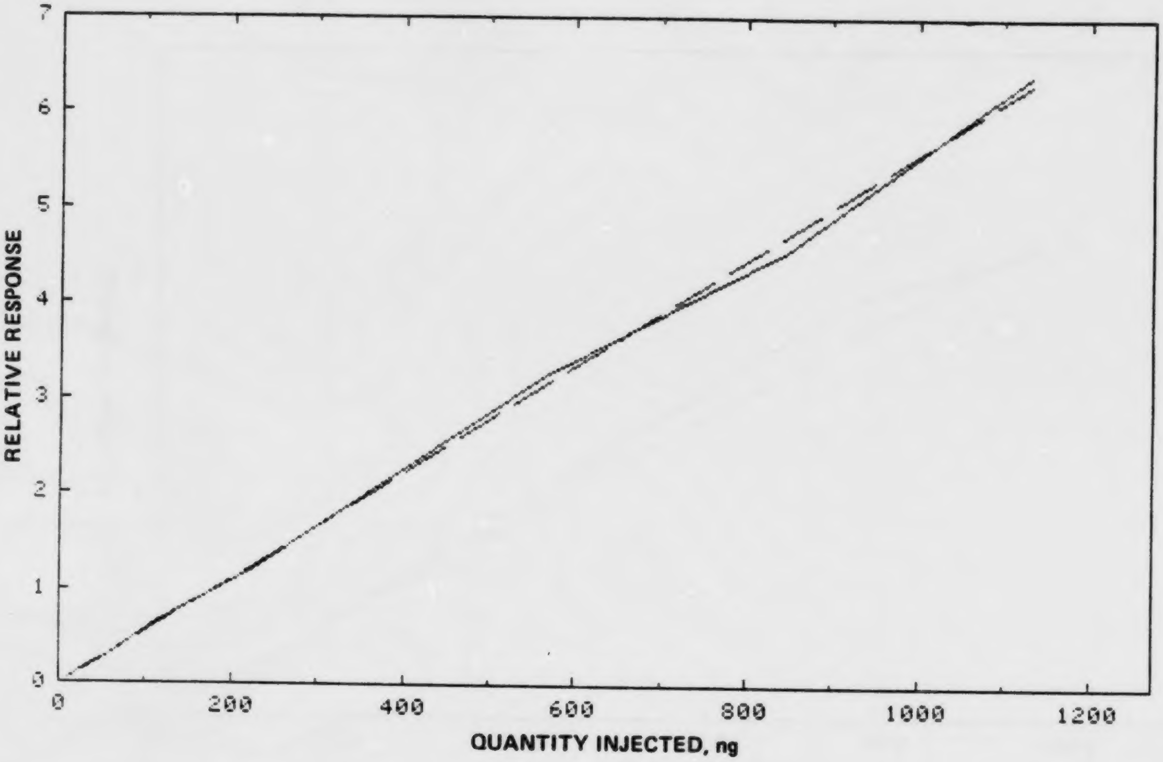

Figure A-17. Calibration curve for the determination of pentachloronitrobenzene by GC/FID.

Range: 11 - 1100 ng
Correlation coefficient: 0.999
Slope: 5.6×10^{-3}
y-Intercept: -1.4×10^{-2}

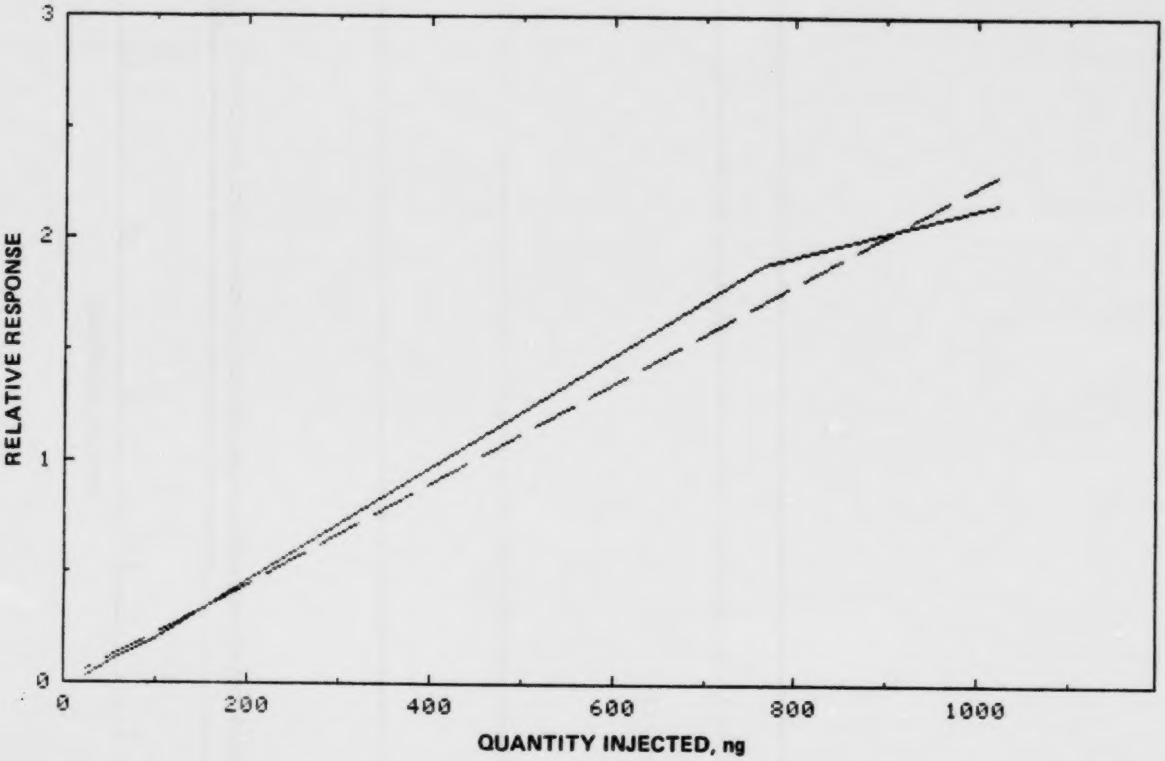

Figure A-18. Calibration curve for the determination of methoxychlor by GC/FID.

Range: 51 - 1000 ng
Correlation coefficient: 0.995
Slope: 2.2×10^{-3}
y-Intercept: -5.1×10^{-4}

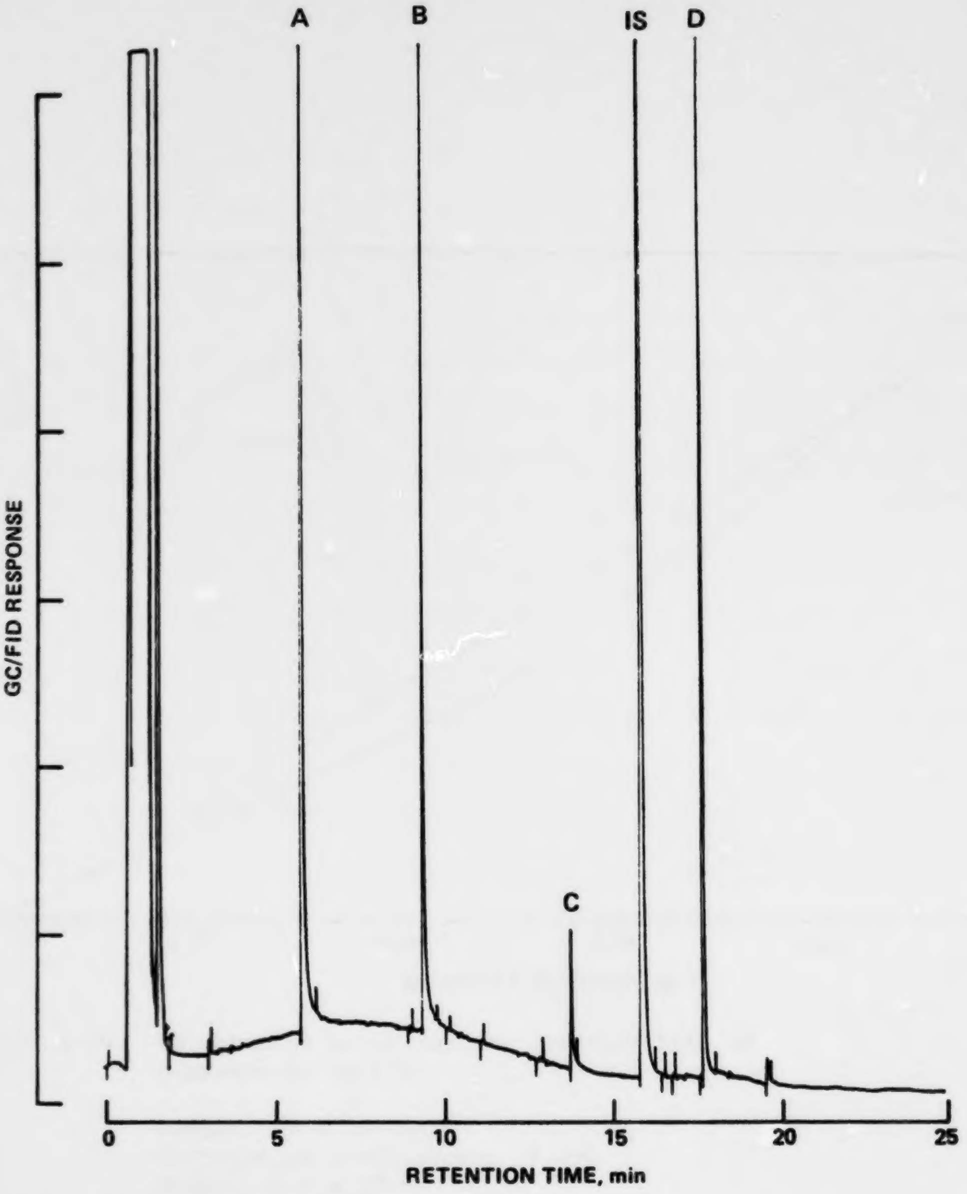

Figure A-19. Chromatogram by GC/FID for

(A) o-cresol(t_R = 5.9 min),
(B) p-chloro-m-cresol(t_R = 9.5 min),
(C) 4,6-dinitro-o-cresol(t_R = 13.9 min), and
(D) dibutyl phthalate(t_R = 17.8 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

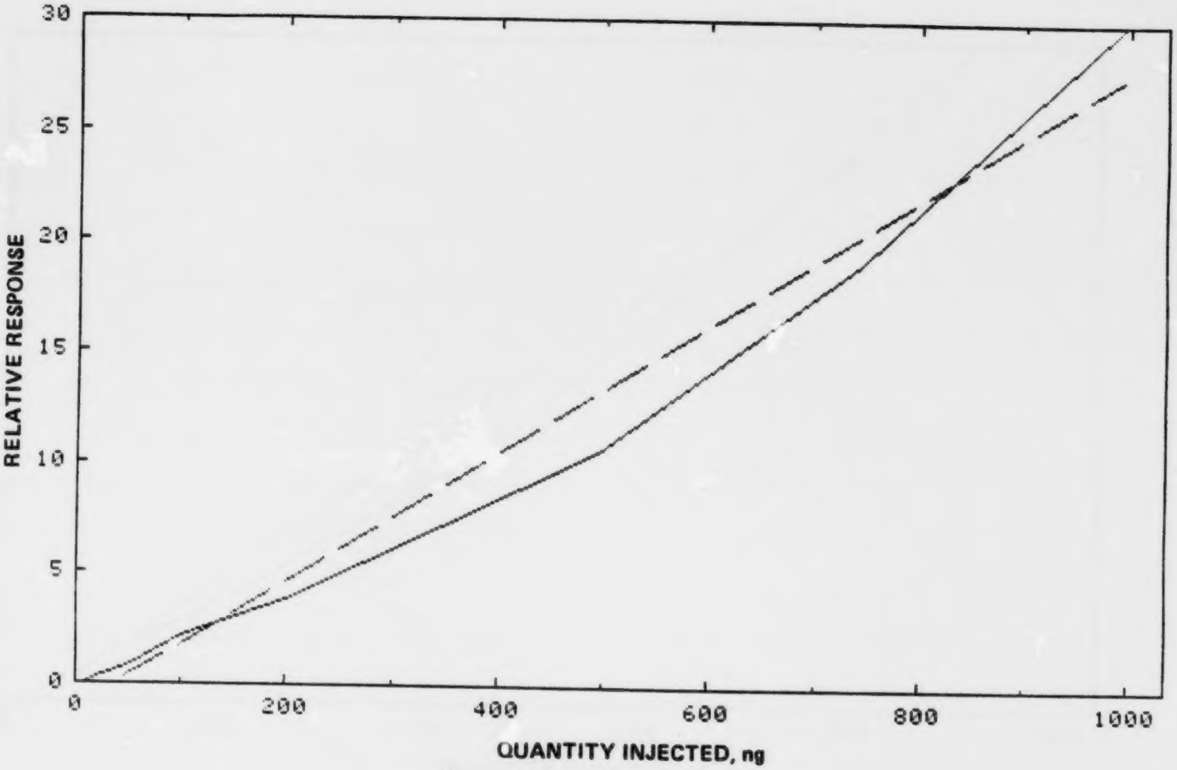

Figure A-20. Calibration curve for the determination of o-cresol by GC/FID.

Range: 99 - 990 ng
Correlation coefficient: 0.990
Slope: 2.9×10^{-2}
y-Intercept: -1.1×10

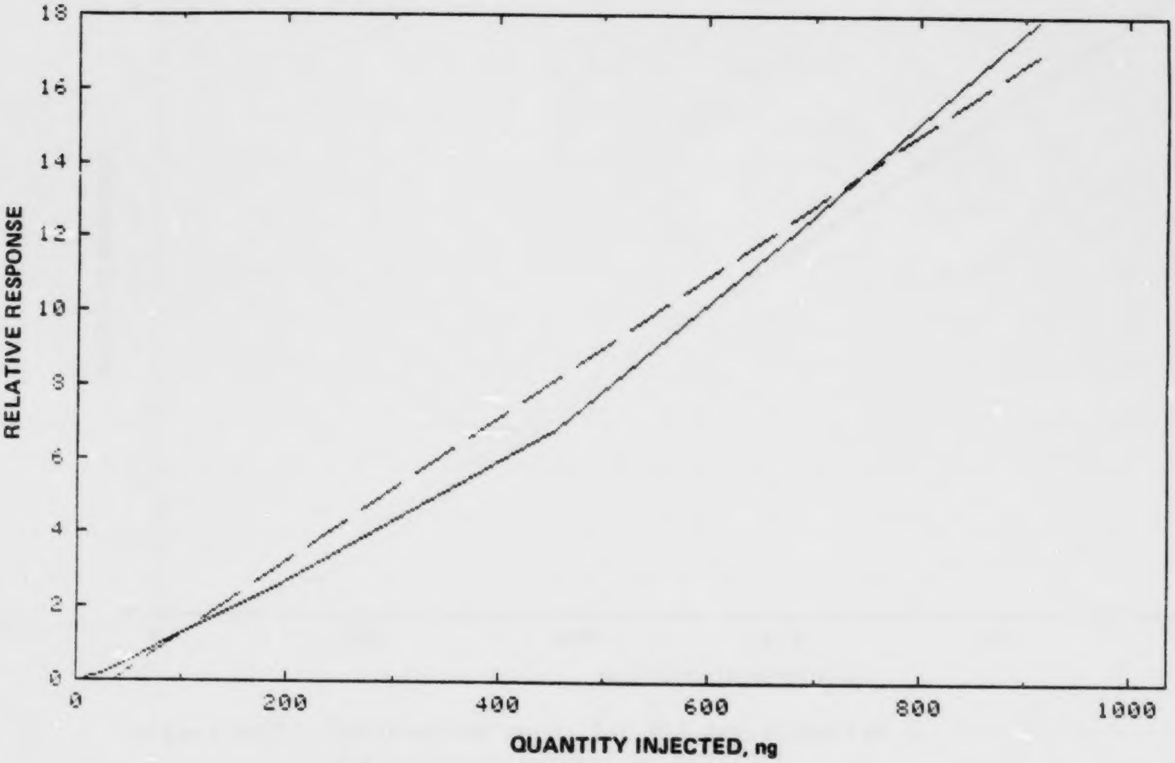

Figure A-21. Calibration curve for the determination of p-chloro-m-cresol by GC/FID.

Range: 91 - 910 ng
Correlation coefficient: 0.994
Slope: 1.9×10^{-2}
y-Intercept: -6.1×10^{-1}

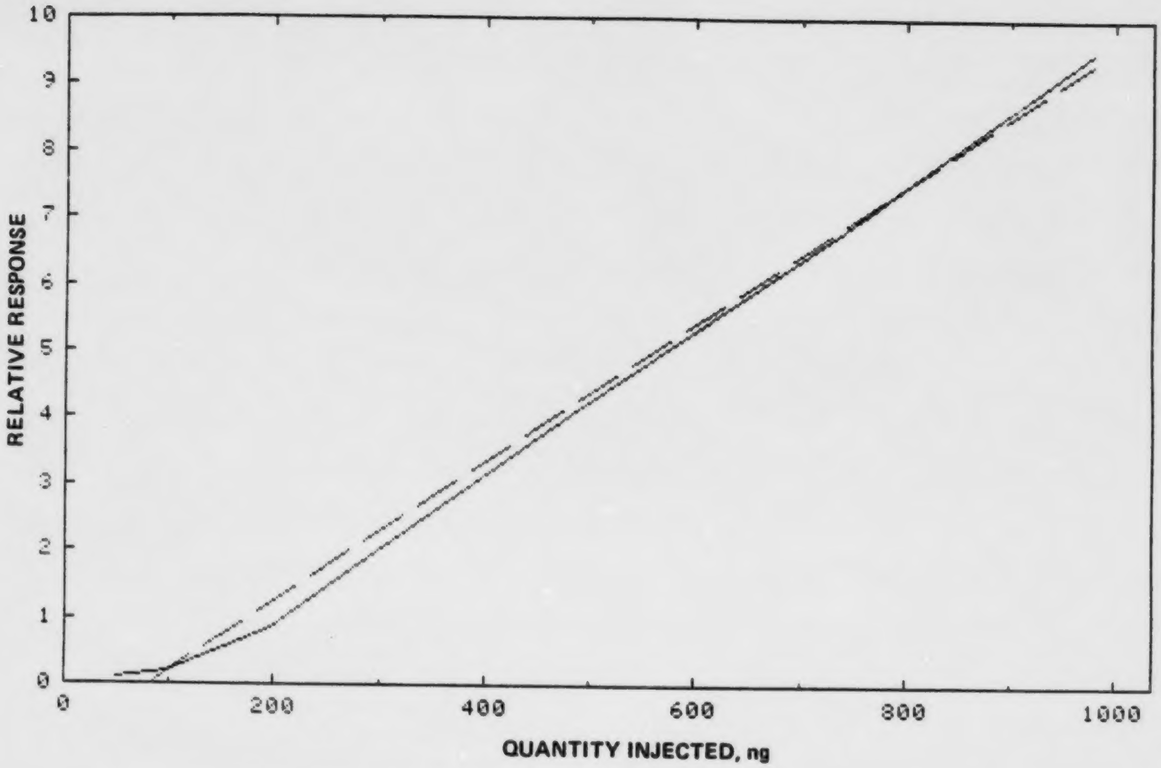

Figure A-22. Calibration curve for the determination of 4,6-dinitro-o-cresol by GC/FID.

Range: 98 - 980 ng
Correlation coefficient: 0.998
Slope: 1.0×10^{-2}
y-Intercept: -8.0×10^{-1}

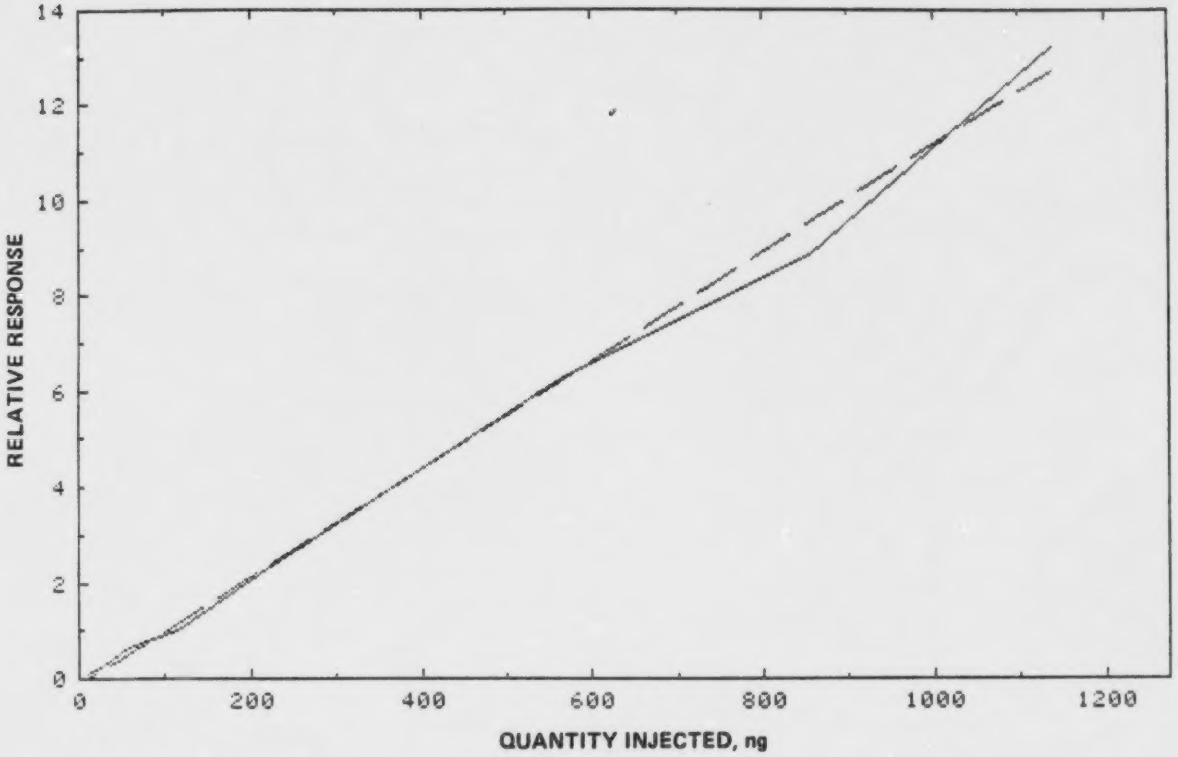

Figure A-23. Calibration curve for the determination of dibutyl phthalate by GC/FID.

Range: 57 - 1100 ng
Correlation coefficient: 0.998
Slope: 1.1×10^{-2}
y-Intercept: -1.3×10^{-1}

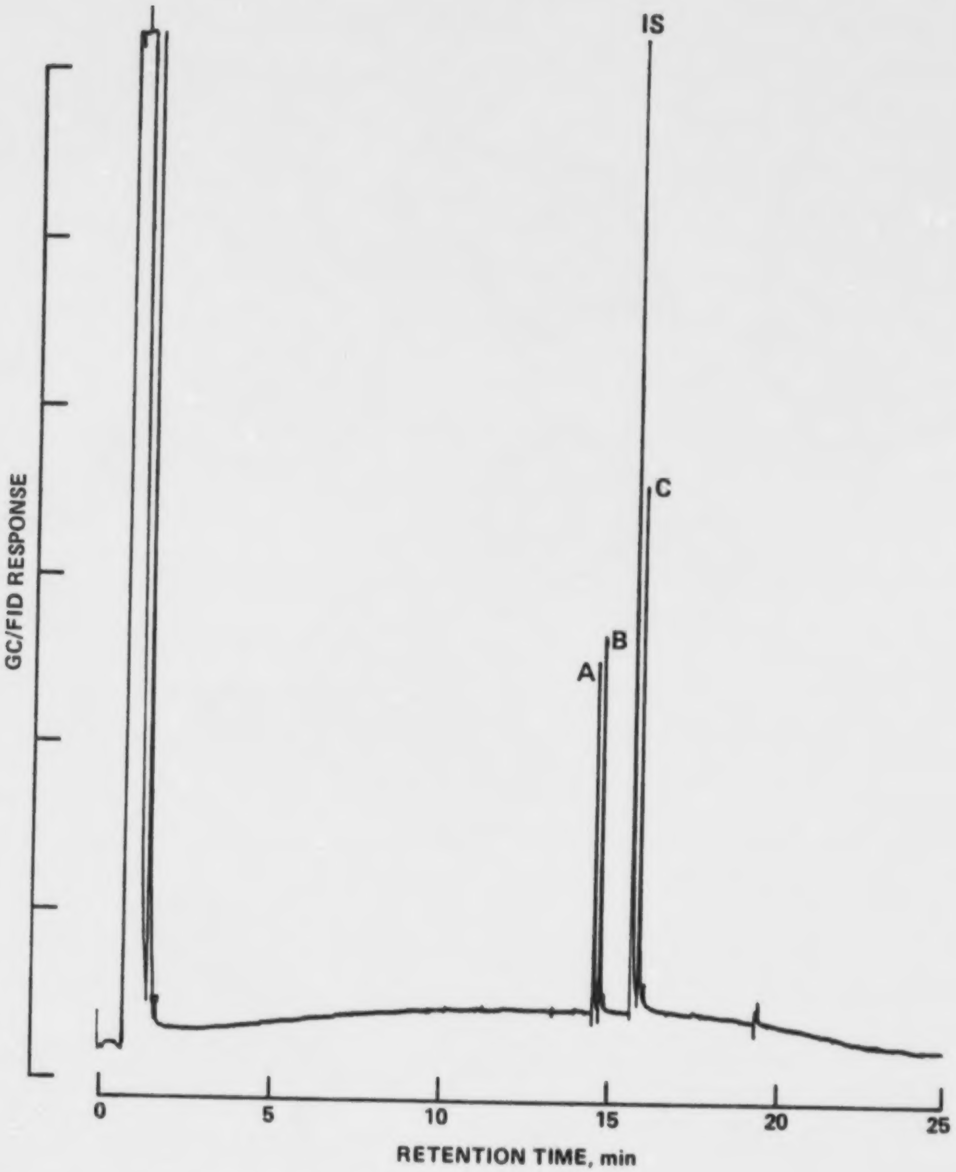

Figure A-24. Chromatogram by GC/FID for

(A) diallate isomer(t_R = 14.8 min),
(B) diallate isomer(t_R = 14.9 min), and
(C) disulfoton(t_R = 16.1 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

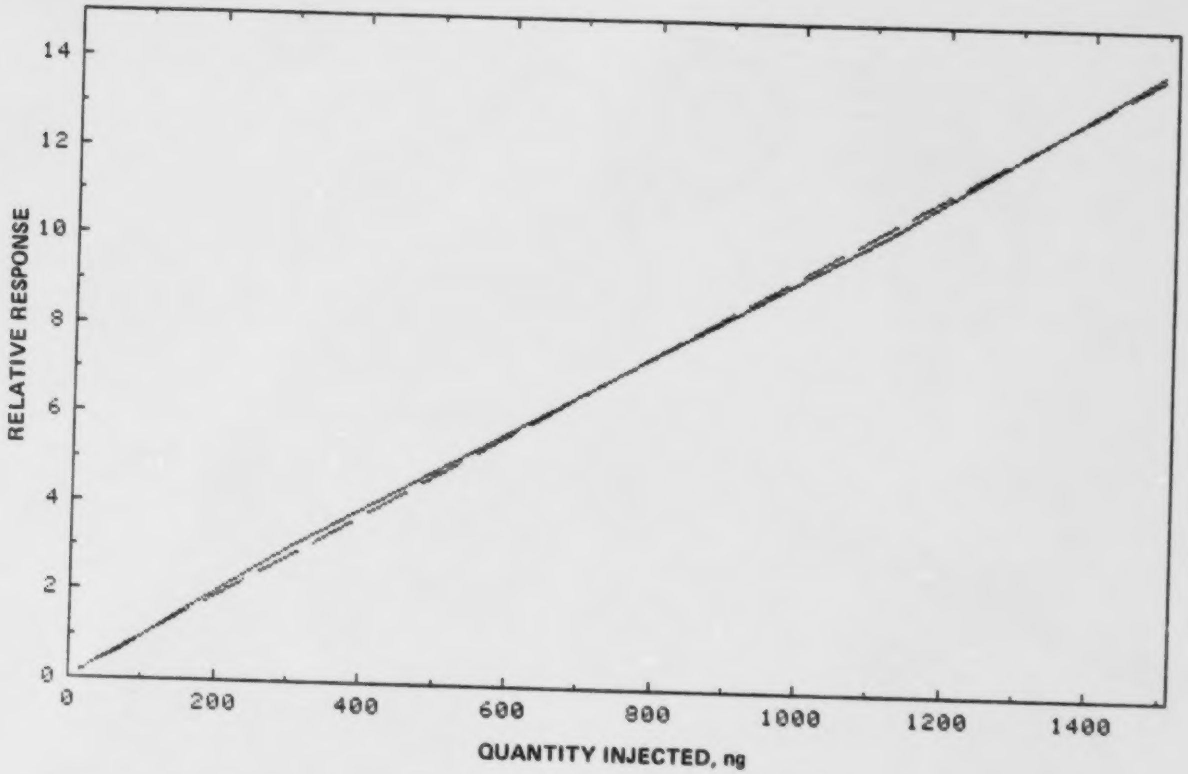

Figure A-25. Calibration curve for the determination of diallate by GC/FID.

Range: 37 - 1500 ng
Correlation coefficient: 0.999
Slope: 9.3×10^{-3}
y-Intercept: 5.4×10^{-2}

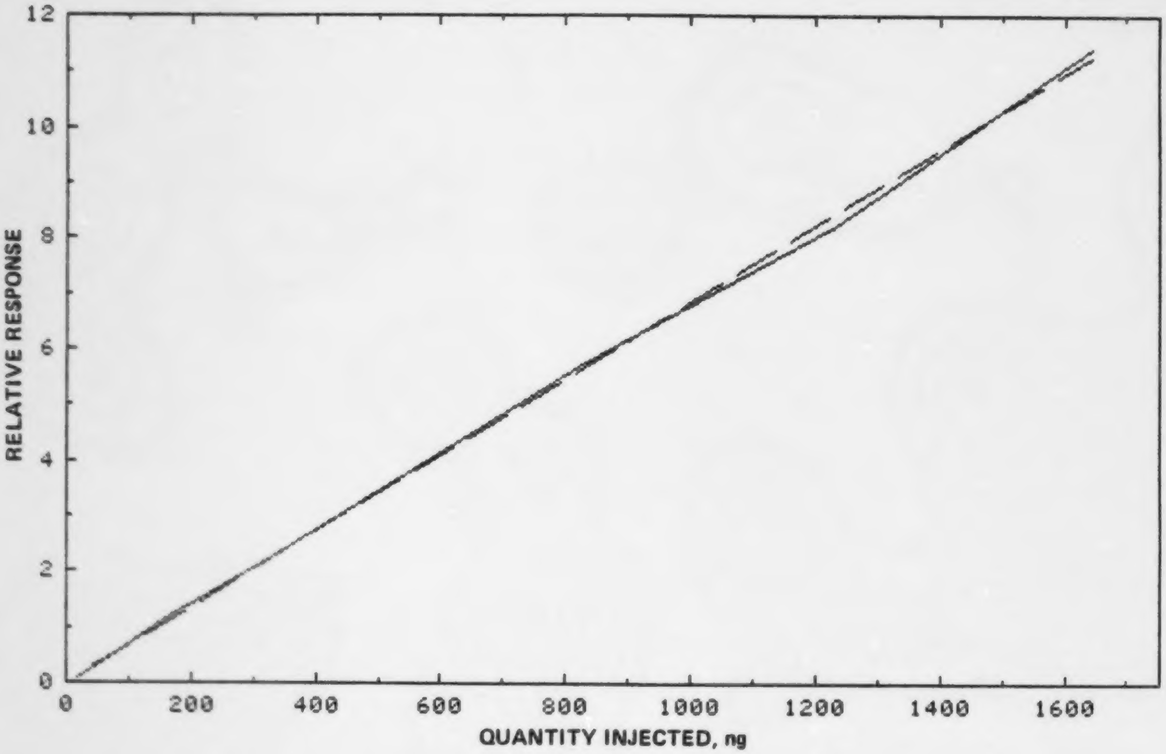

Figure A-26. Calibration curve for the determination of disulfoton by GC/FID.

Range: 16 - 1600 ng
Correlation coefficient: 0.999
Slope: 6.9 x 10^{-3}
y-Intercept: -1.6 x 10^{-2}

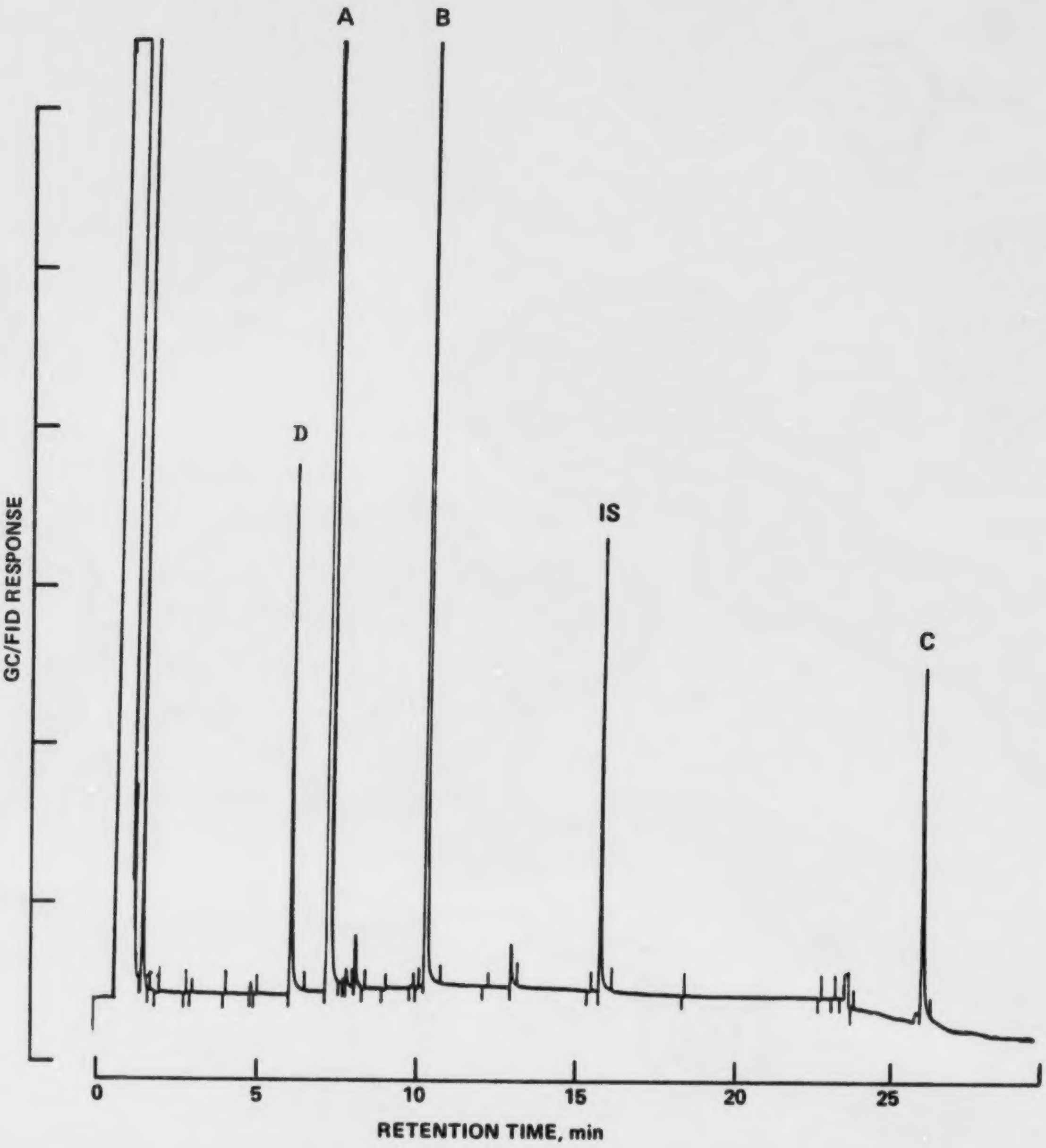

Figure A-27. Chromatogram by GC/FID for

(A) 2,4-dimethylphenol(t_R = 7.4 min),
(B) 2,4,6-trichlorophenol(t_R = 10.4 min),
(C) hexachlorophene(t_R = 26.0 min), and
(D) p-cresol(t_R = 6.2 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

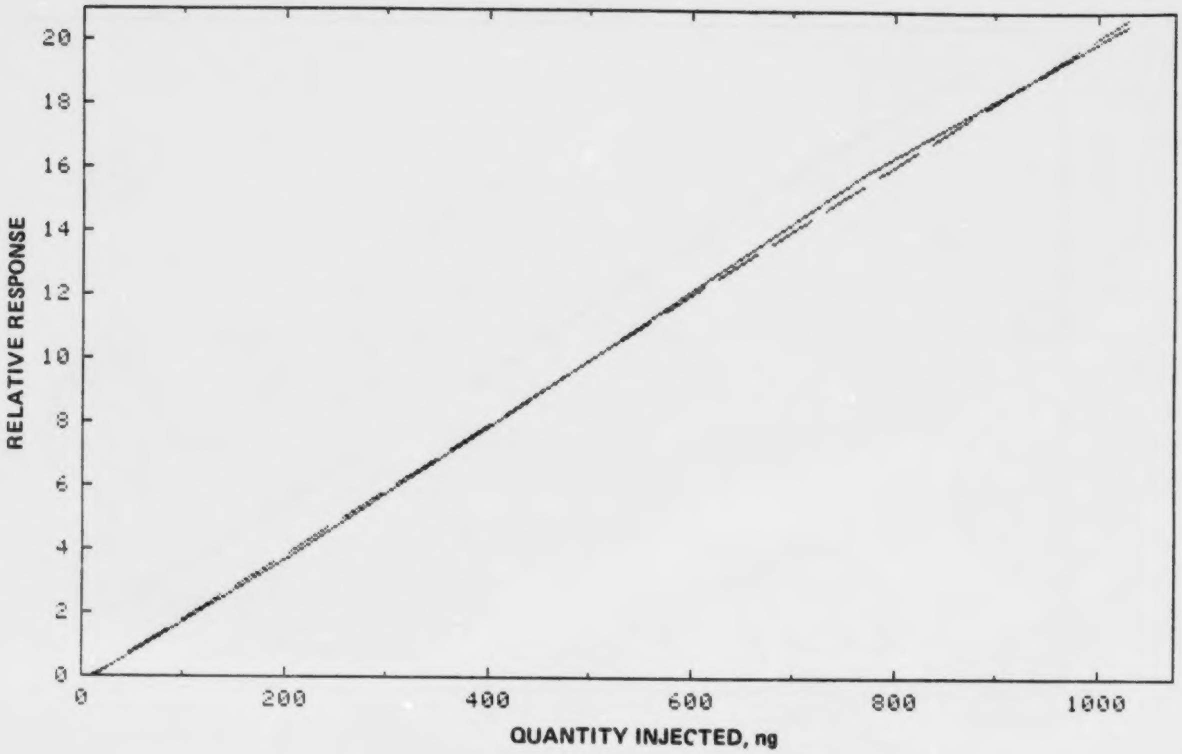

Figure A-28. Calibration curve for the determination of 2,4-dimethylphenol by GC/FID.

Range: 26 - 1000 ng
Correlation coefficient: 0.999
Slope: 2.1×10^{-2}
y-Intercept: -2.6×10^{-1}

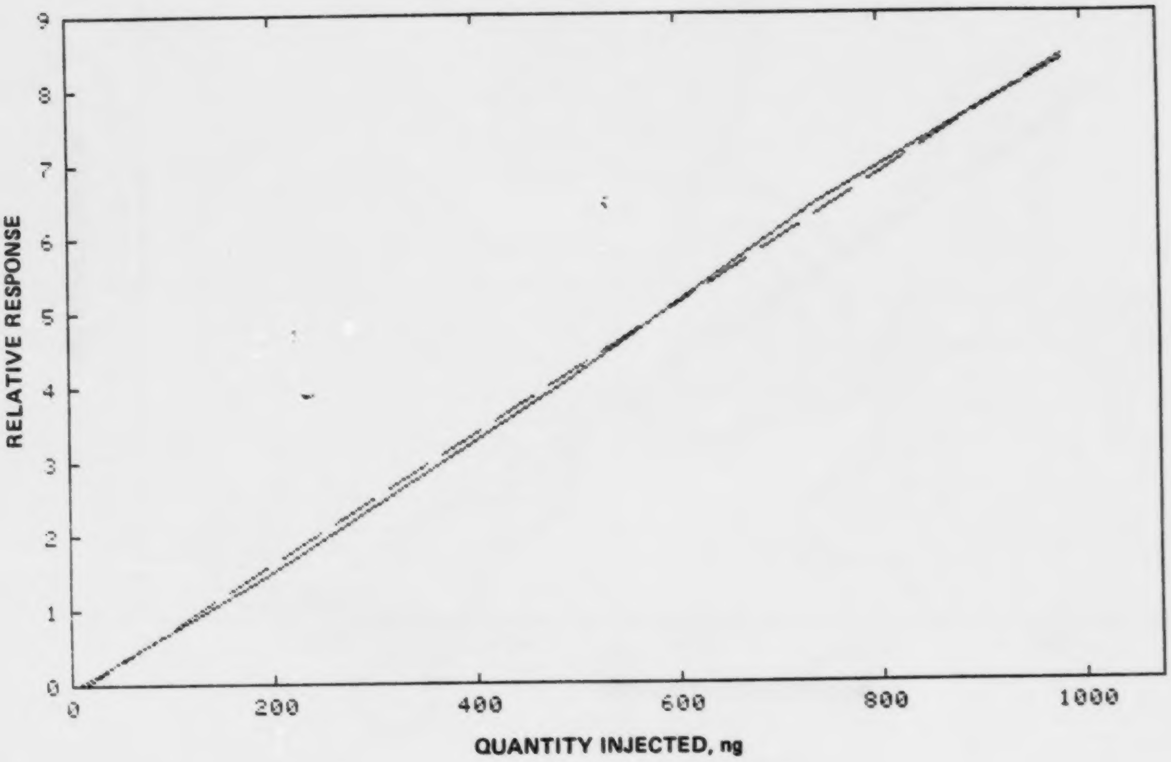

Figure A-29. Calibration curve for the determination of 2,4,6-trichlorophenol by GC/FID.

Range: 49 - 980 ng
Correlation coefficient: 0.999
Slope: 8.7×10^{-3}
y-Intercept: -1.2×10^{-1}

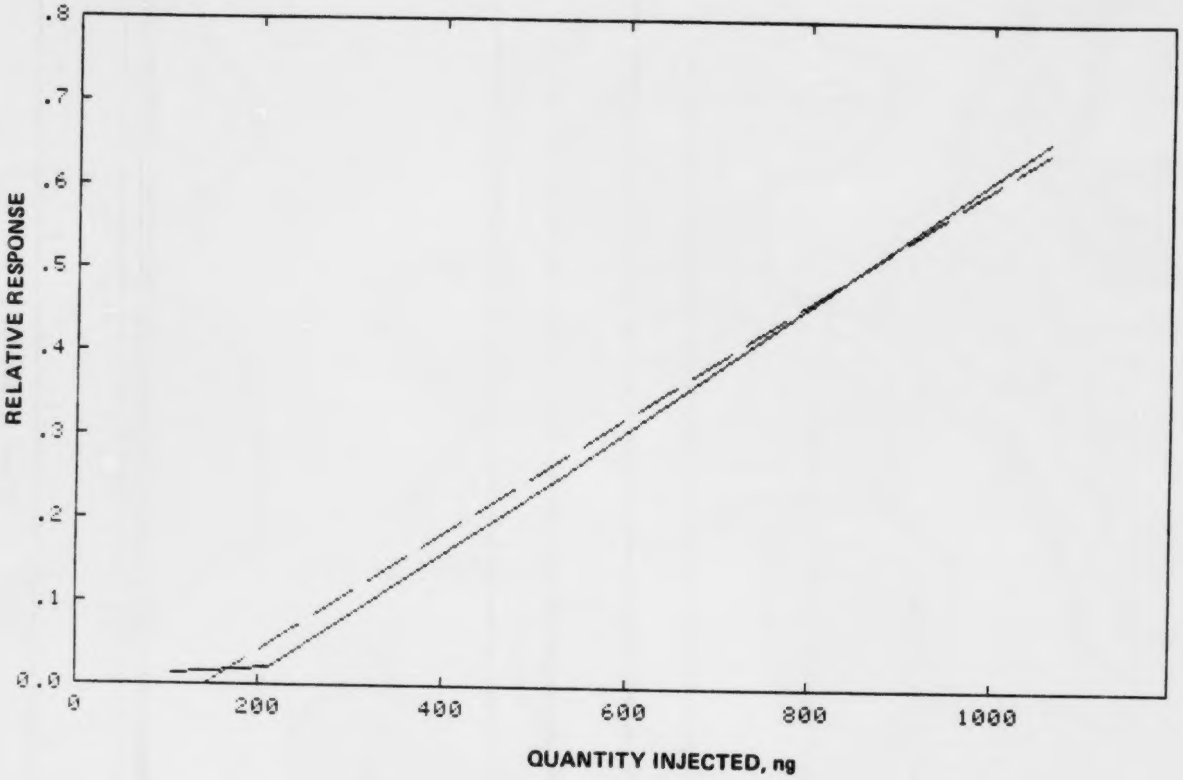

Figure A-30. Calibration curve for the determination of hexachlorophene by GC/FID.

Range: 530 - 1100 ng
Correlation coefficient: 0.995
Slope: 7.0×10^{-4}
y-Intercept: -9.9×10^{-2}

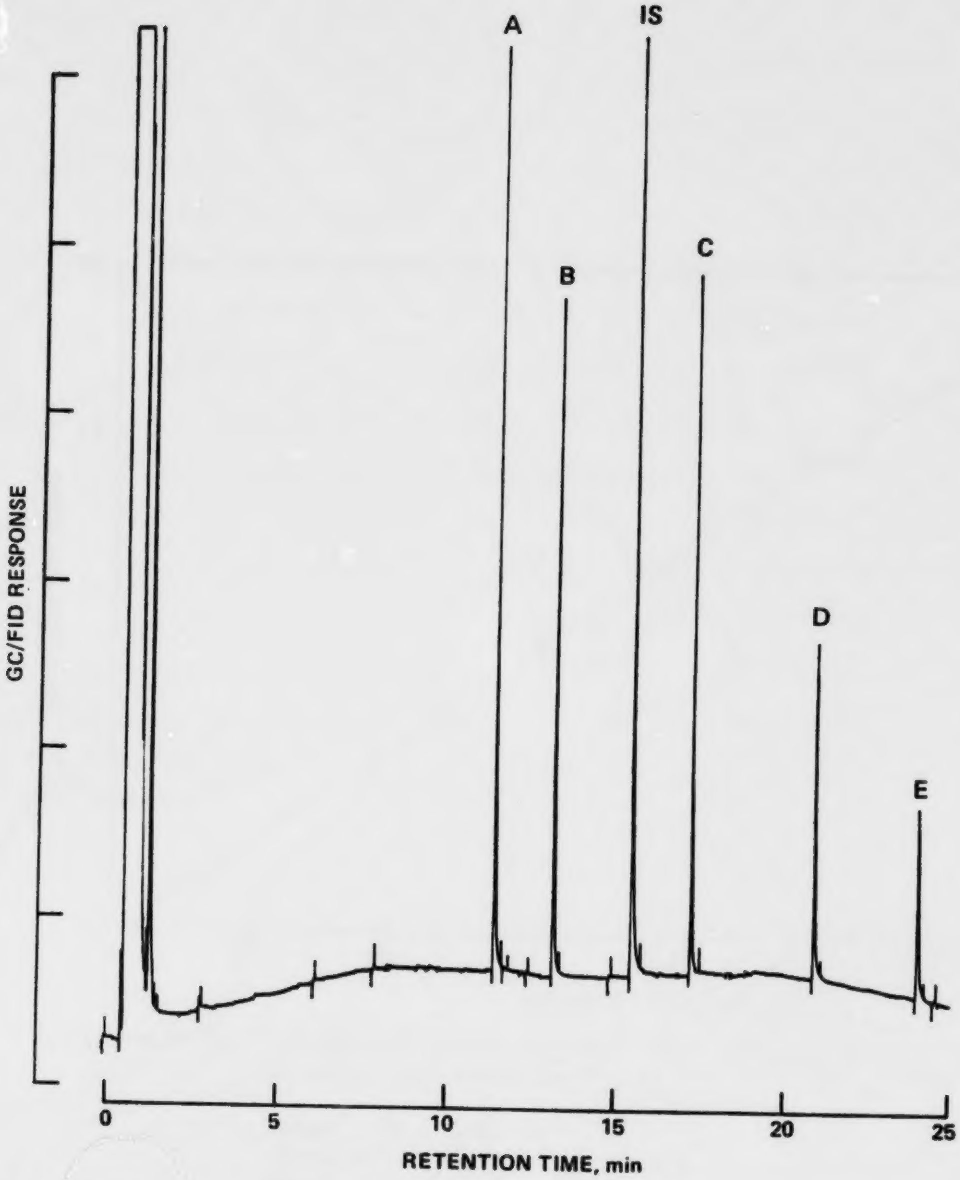

Figure A-31. Chromatogram by GC/FID for

(A) dimethyl phthalate(t_R = 11.8 min),
(B) diethyl phthalate(t_R = 13.6 min),
(C) diisobutyl phthalate(t_R = 17.7 min),
(D) butylbenzyl phthalate(t_R = 21.4 min), and
(E) dioctyl phthalate(t_R = 24.4 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

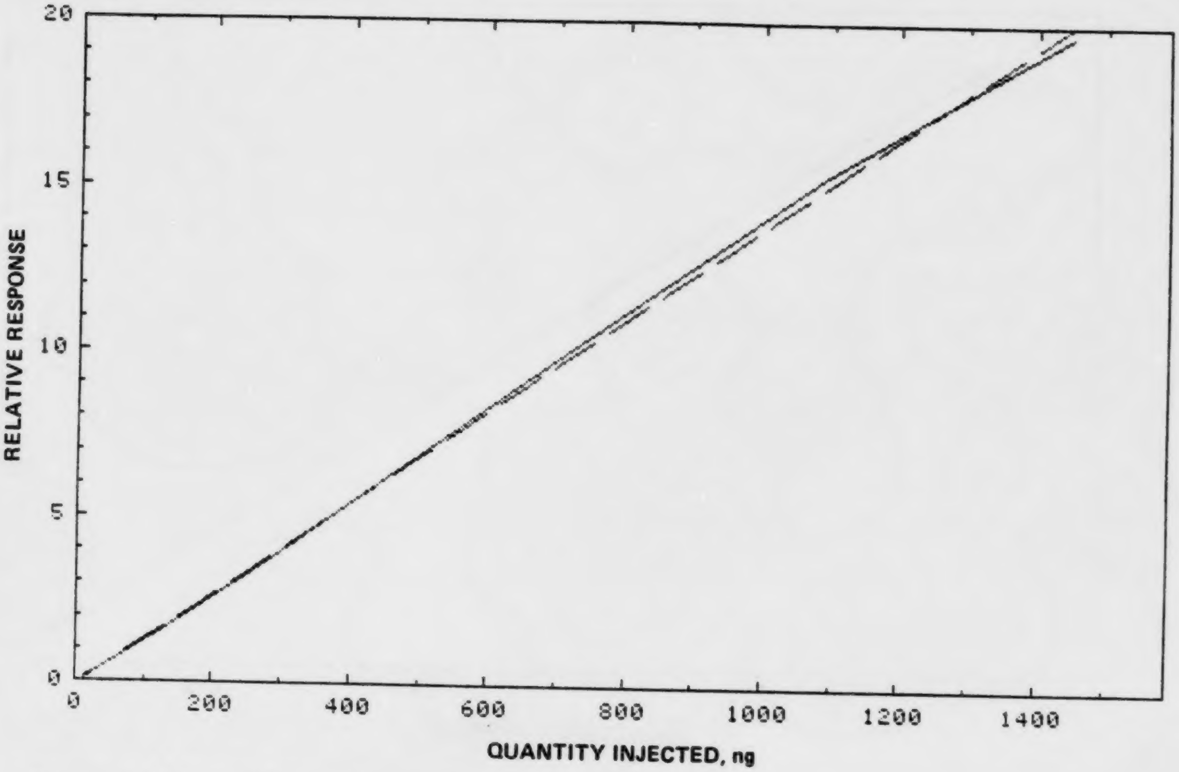

Figure A-32. Calibration curve for the determination of dimethyl phthalate by GC/FID.

Range: 36 - 1400 ng
Correlation coefficient: 0.999
Slope: 1.4×10^{-2}
y-Intercept: -1.1×10^{-1}

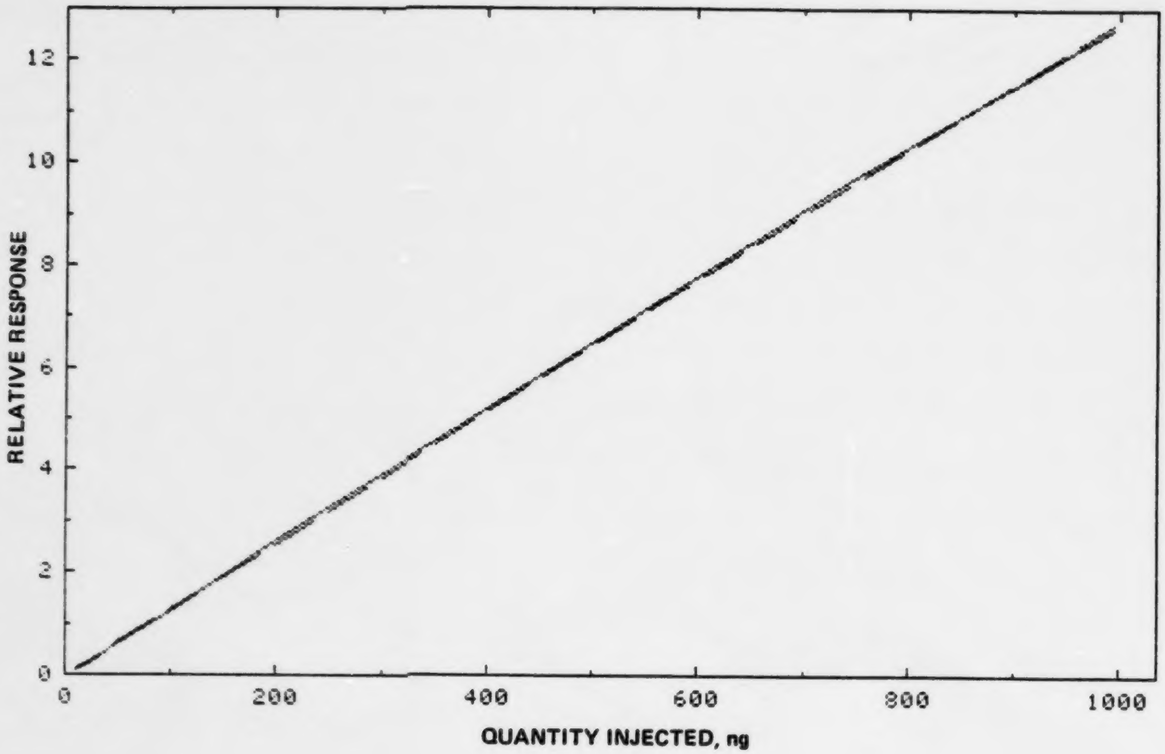

Figure A-33. Calibration curve for the determination of diethyl phthalate by GC/FID.

Range: 9.9 - 990 ng
Correlation coefficient: 0.999
Slope: 1.3×10^{-2}
y-Intercept: -6.0×10^{-3}

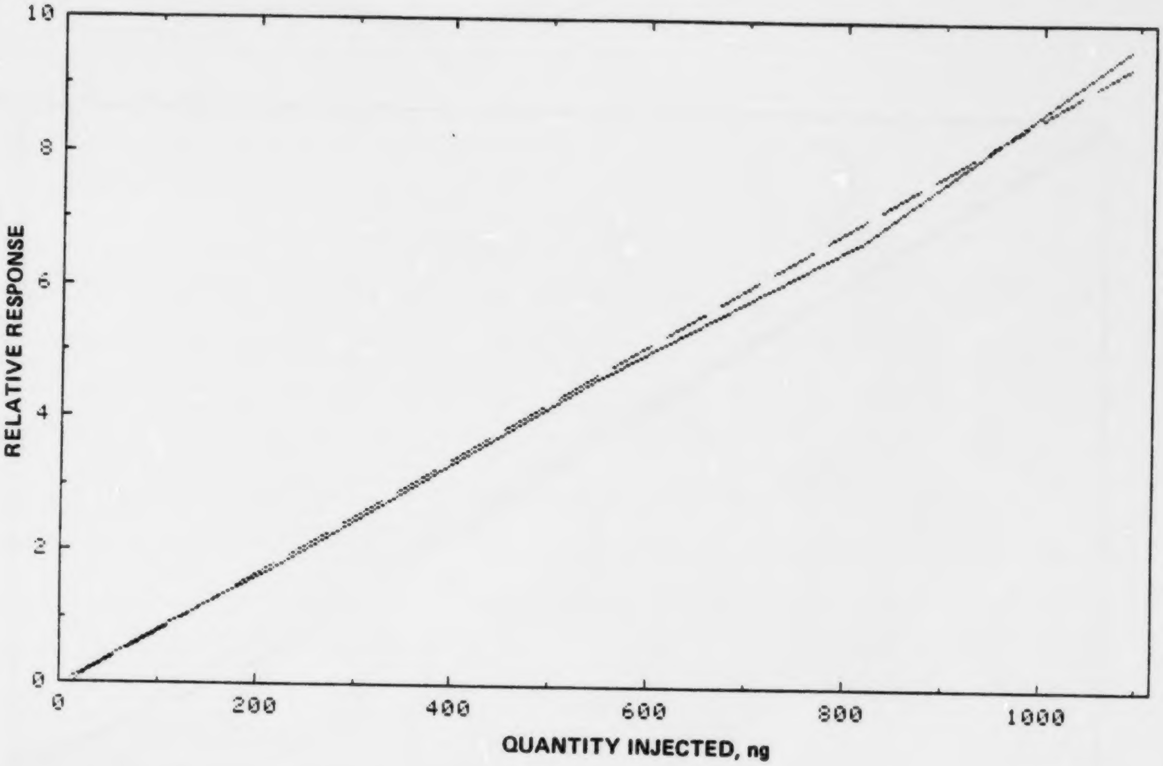

Figure A-34. Calibration curve for the determination of diisobutyl phthalate by GC/FID.

Range: 27 - 1100 ng
Correlation coefficient: 0.999
Slope: 8.7×10^{-3}
y-Intercept: -8.4×10^{-2}

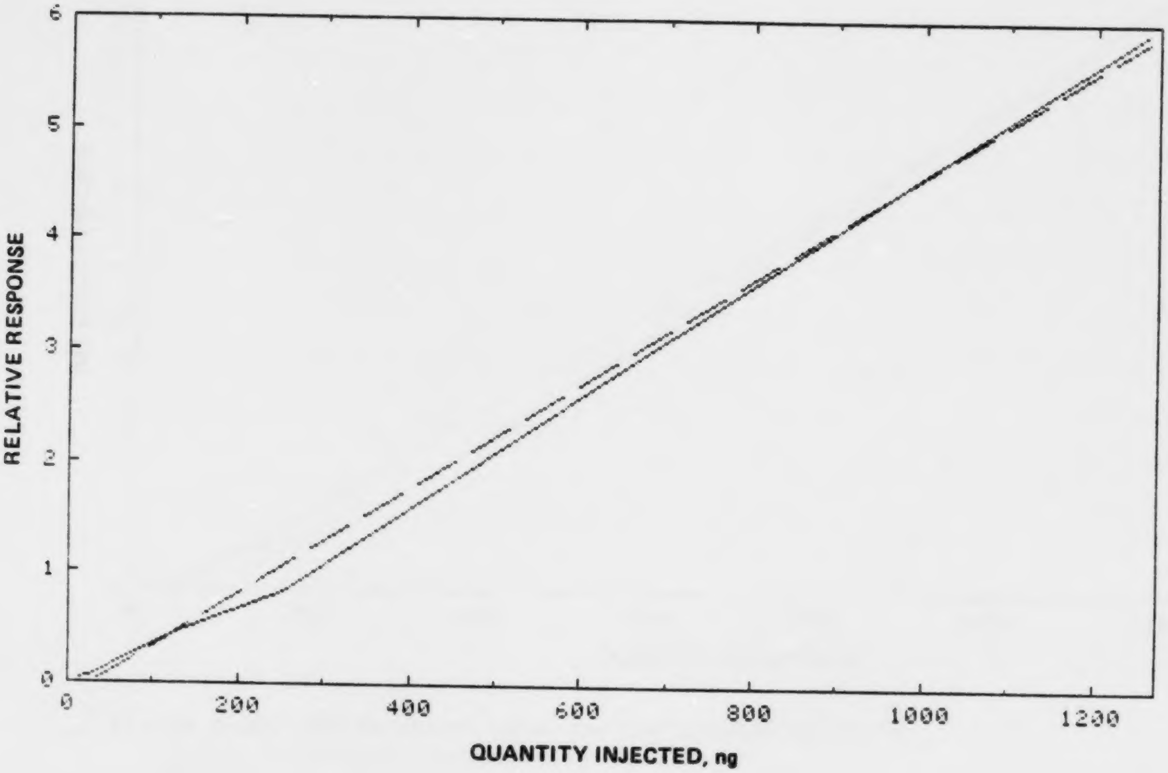

Figure A-35. Calibration curve for the determination of butylbenzyl phthalate by GC/FID.

Range: 130 - 1300 ng
Correlation coefficient: 0.998
Slope: 4.8 x 10^{-3}
y-Intercept: -1.4 x 10^{-1}

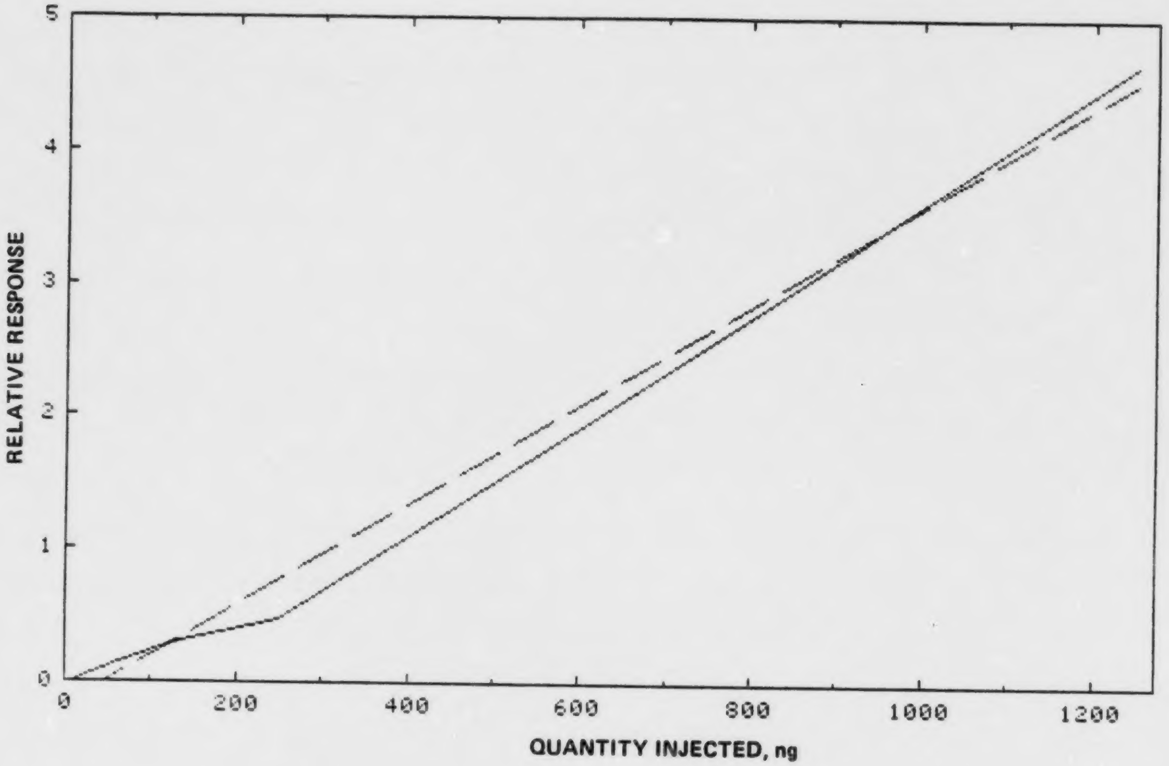

Figure A-36. Calibration curve for the determination of dioctyl phthalate by GC/FID.

Range: 120 - 1200 ng
Correlation coefficient: 0.954
Slope: 3.3×10^{-3}
y-Intercept: -1.4×10^{-1}

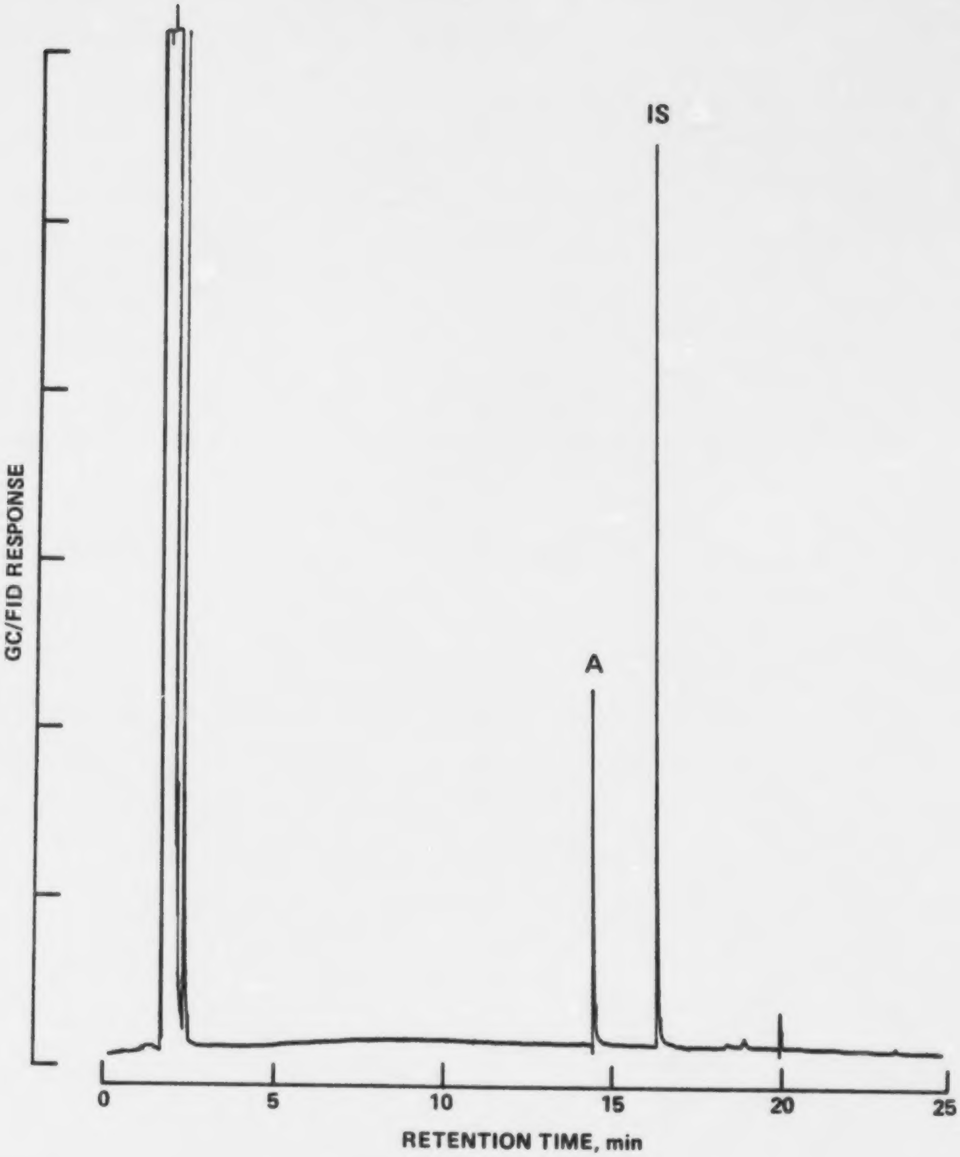

Figure A-37. Chromatogram by GC/FID for diphenylamine (t_R = 13.9 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

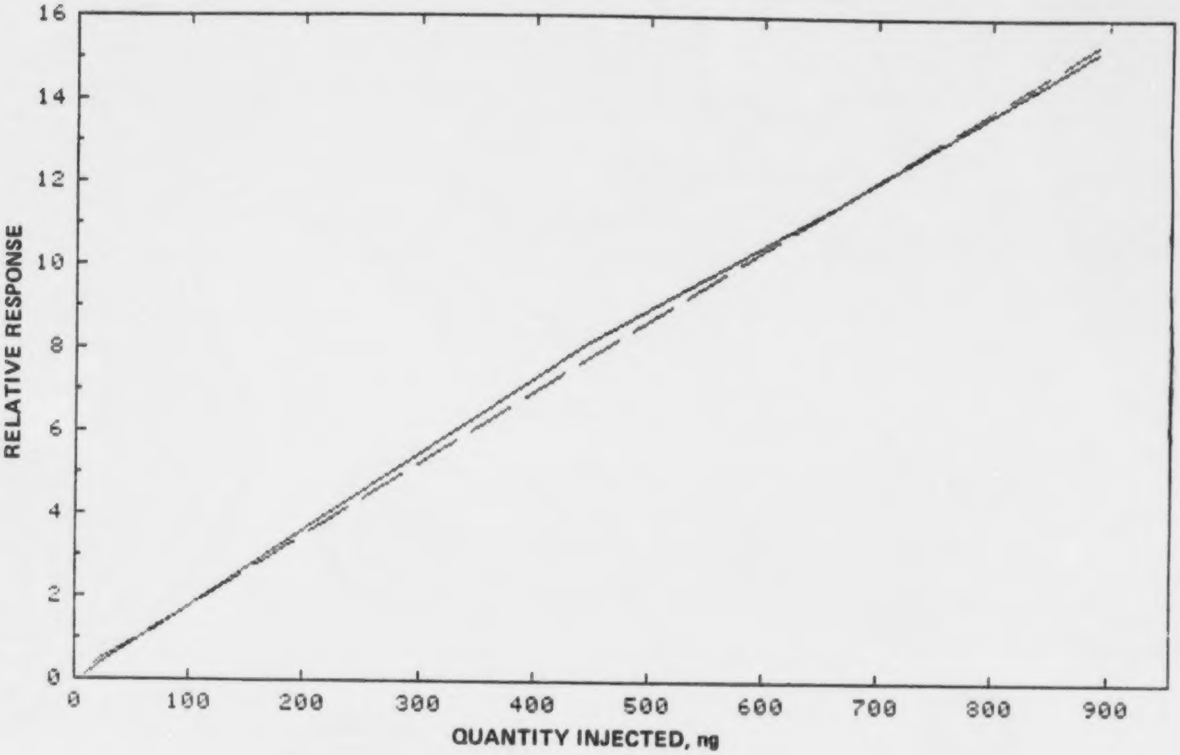

Figure A-38. Calibration curve for the determination of diphenylamine by GC/FID.

Range: 22 - 890 ng
Correlation coefficient: 0.999
Slope: 1.7×10^{-2}
y-Intercept: 6.7×10^{-2}

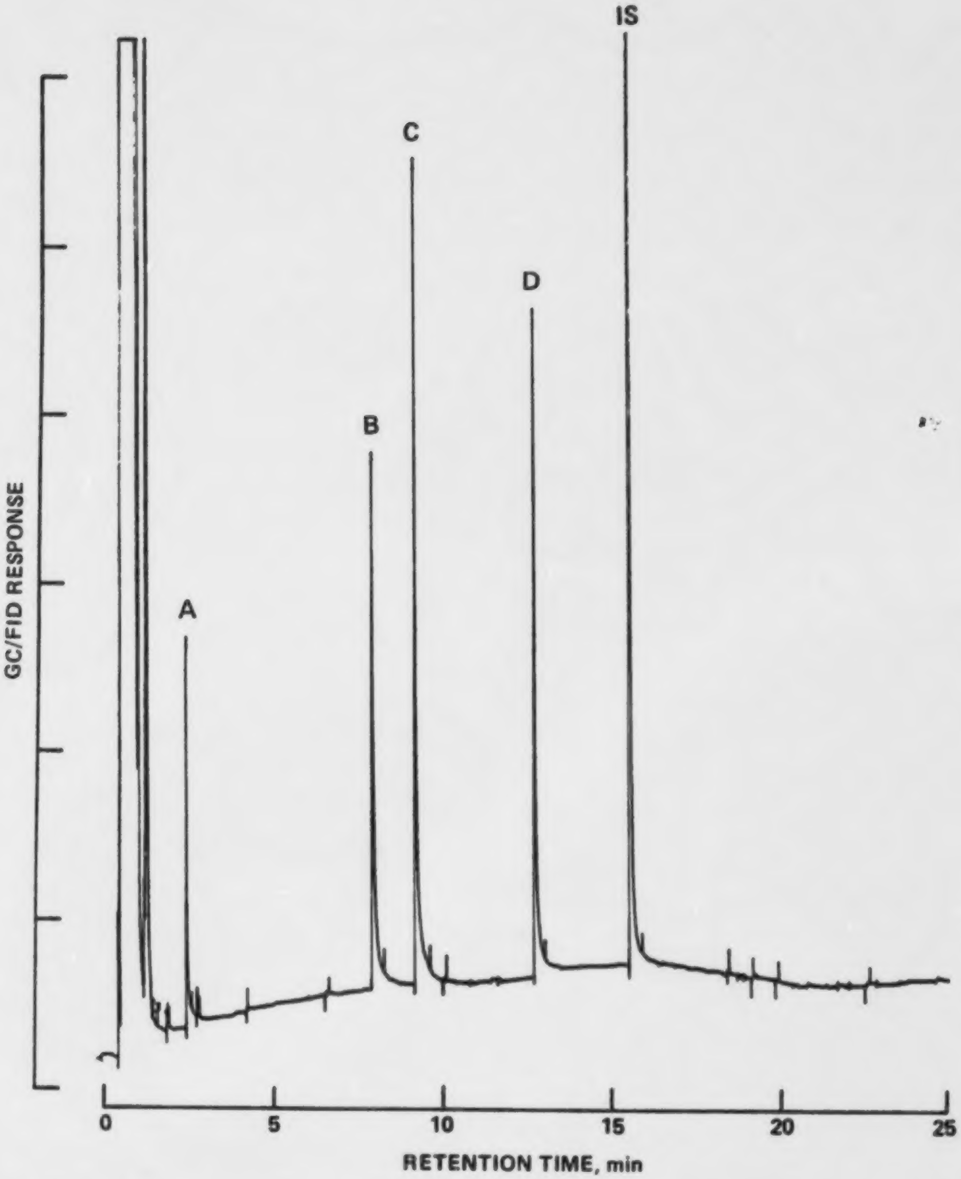

Figure A-39. Chromatogram by GC/FID for

(A) ethyl carbamate(t_R = 2.9 min),
(B) o-phenylenediamine(t_R = 8.3 min),
(C) m-phenylenediamine(t_R = 9.6 min), and
(D) 2-naphthylamine(t_R = 13.0 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

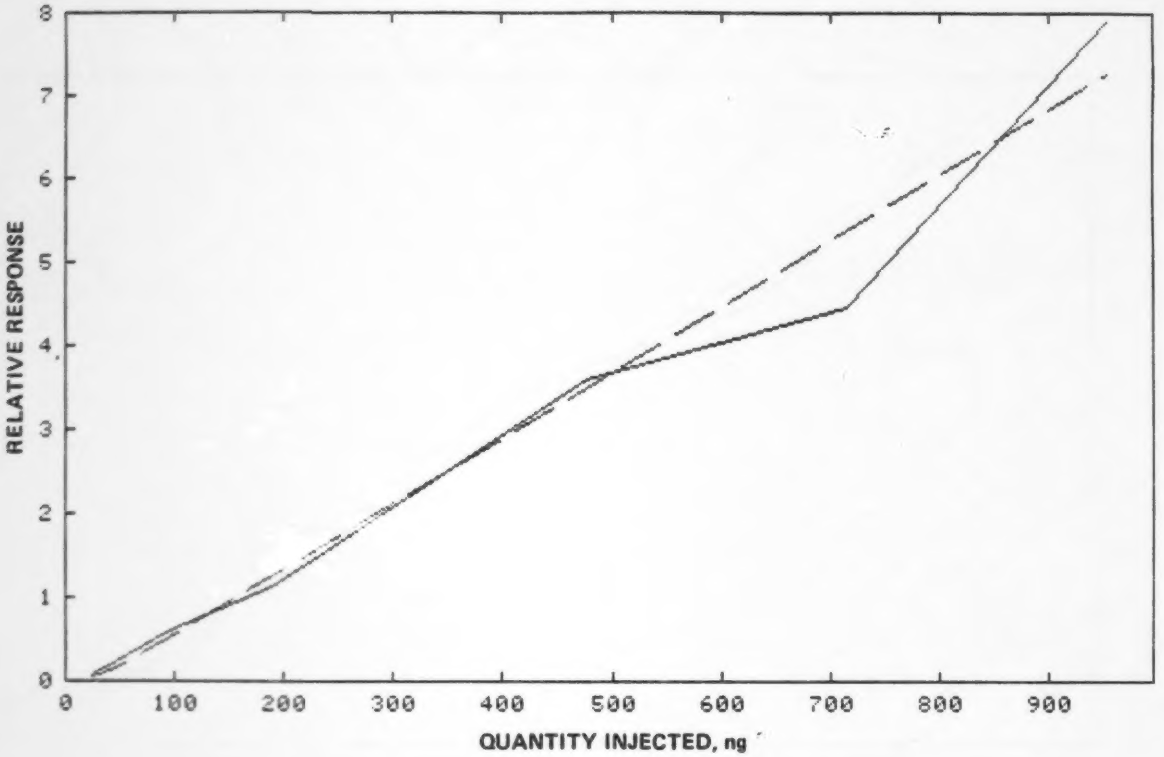

Figure A-40. Calibration curve for the determination of ethyl carbamate by GC/FID.

Range: 24 - 950 ng
Correlation coefficient: 0.987
Slope: 7.9×10^{-3}
y-Intercept: -2.3×10^{-1}

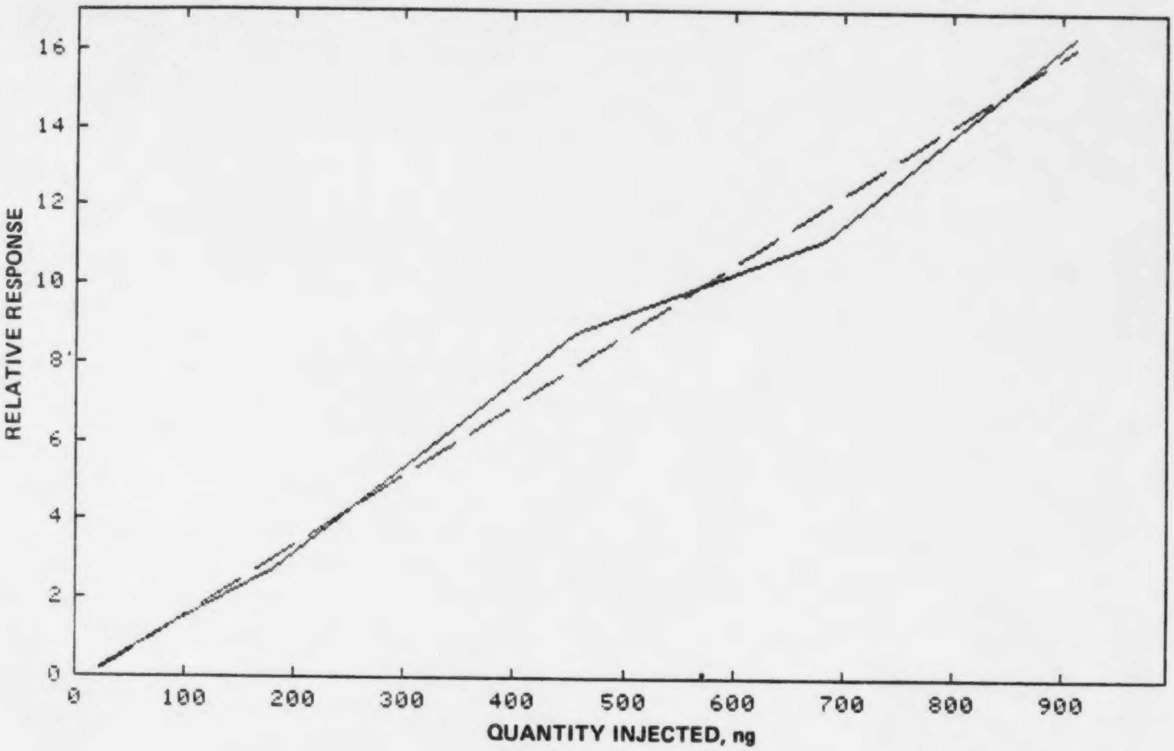

Figure A-41. Calibration curve for the determination of o-phenylenediamine by GC/FID.

Range: 23 - 910 ng
Correlation coefficient: 0.997
Slope: 1.8×10^{-2}
y-Intercept: -2.3×10^{-1}

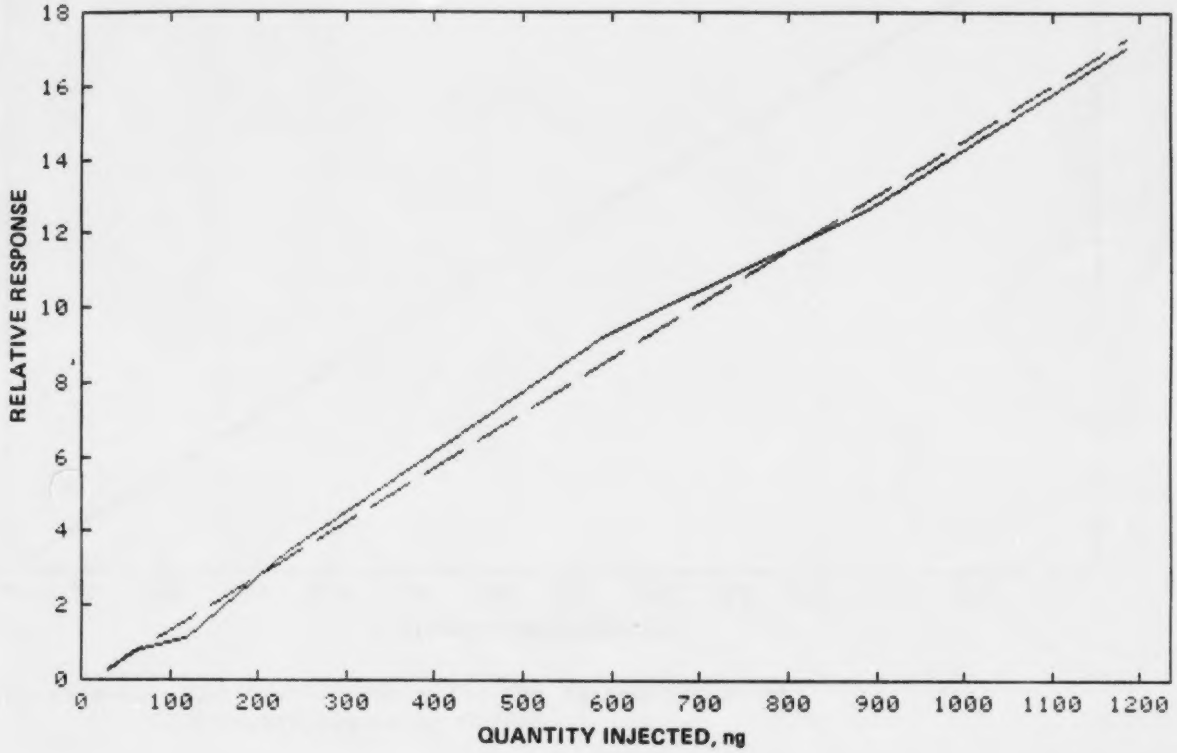

Figure A-42. Calibration curve for the determination of m-phenylenediamine by GC/FID.

Range: 30 - 1200 ng
Correlation coefficient: 0.998
Slope: 1.5 x 10^{-2}
y-Intercept: -1.5 x 10^{-1}

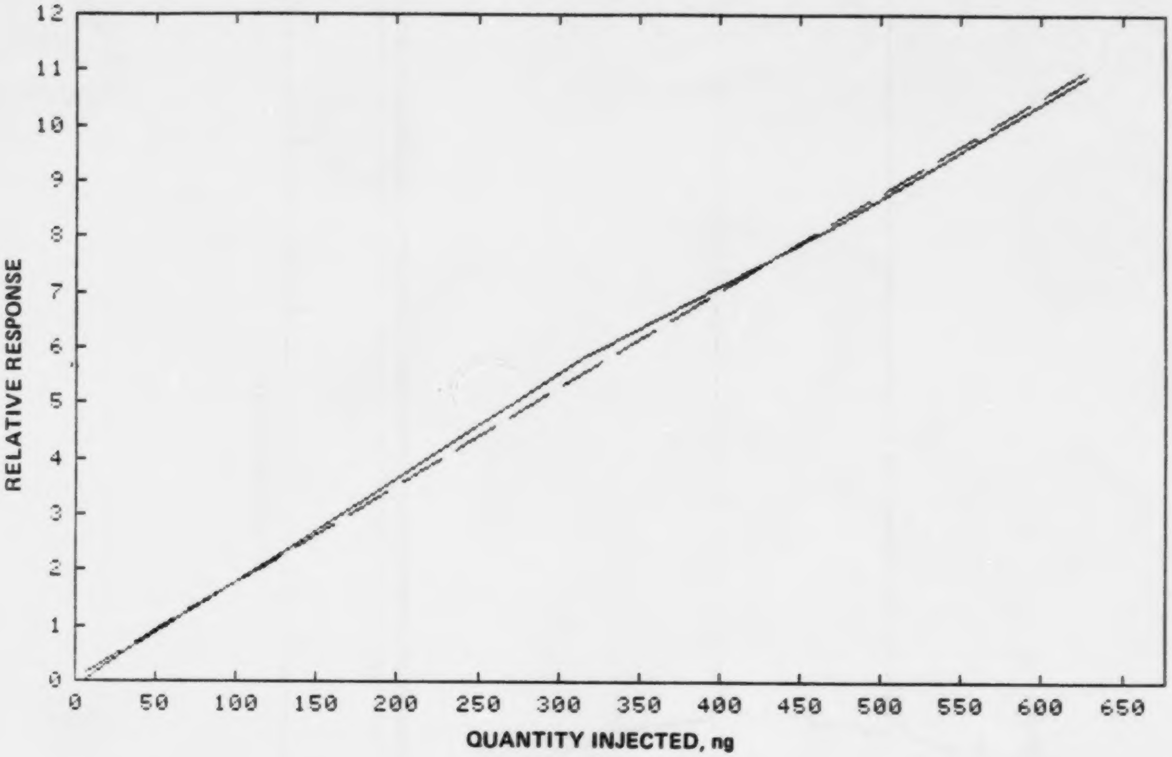

Figure A-43. Calibration curve for the determination of 2-naphthylamine by GC/FID.

Range: 31 - 630 ng
Correlation coefficient: 0.999
Slope: 1.8×10^{-2}
y-Intercept: 2.8×10^{-2}

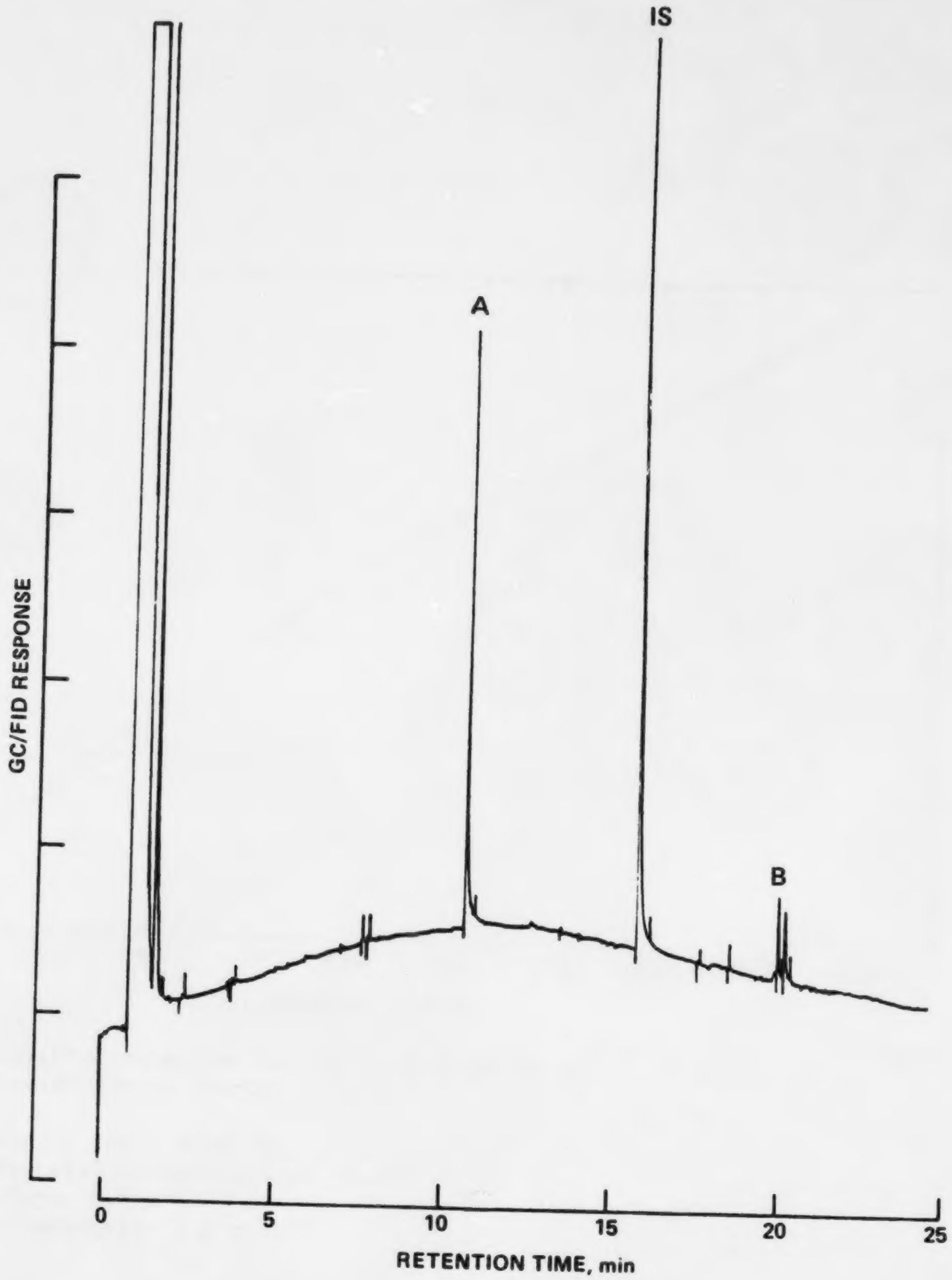

Figure A-44. Chromatogram by GC/FID for

(A) isosafrole(t_R = 10.8 min) and
(B) aramite isomers(t_R = 20.2 min and 20.4 min)

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

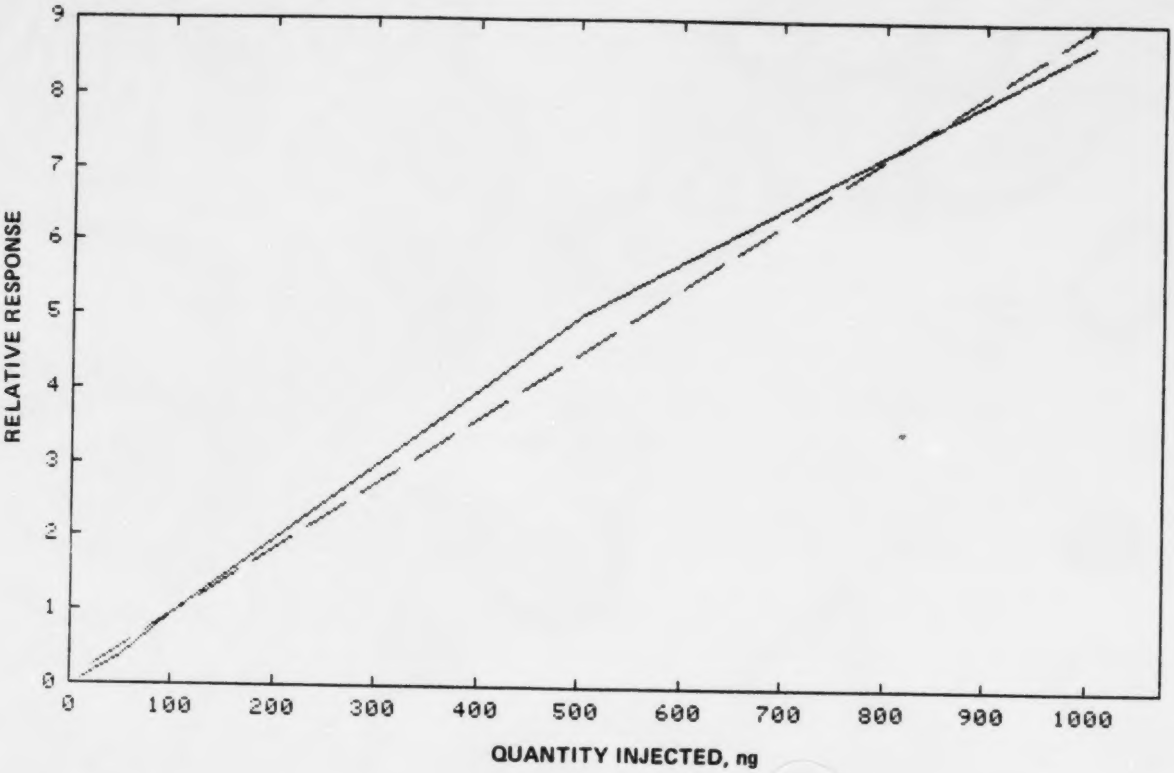

Figure A-45. Calibration curve for the determination of isosafrole by GC/FID.

Range: 100 - 1000 ng
Correlation coefficient: 0.997
Slope: 8.9 x 10^{-3}
y-Intercept: 5.8 x 10^{-2}

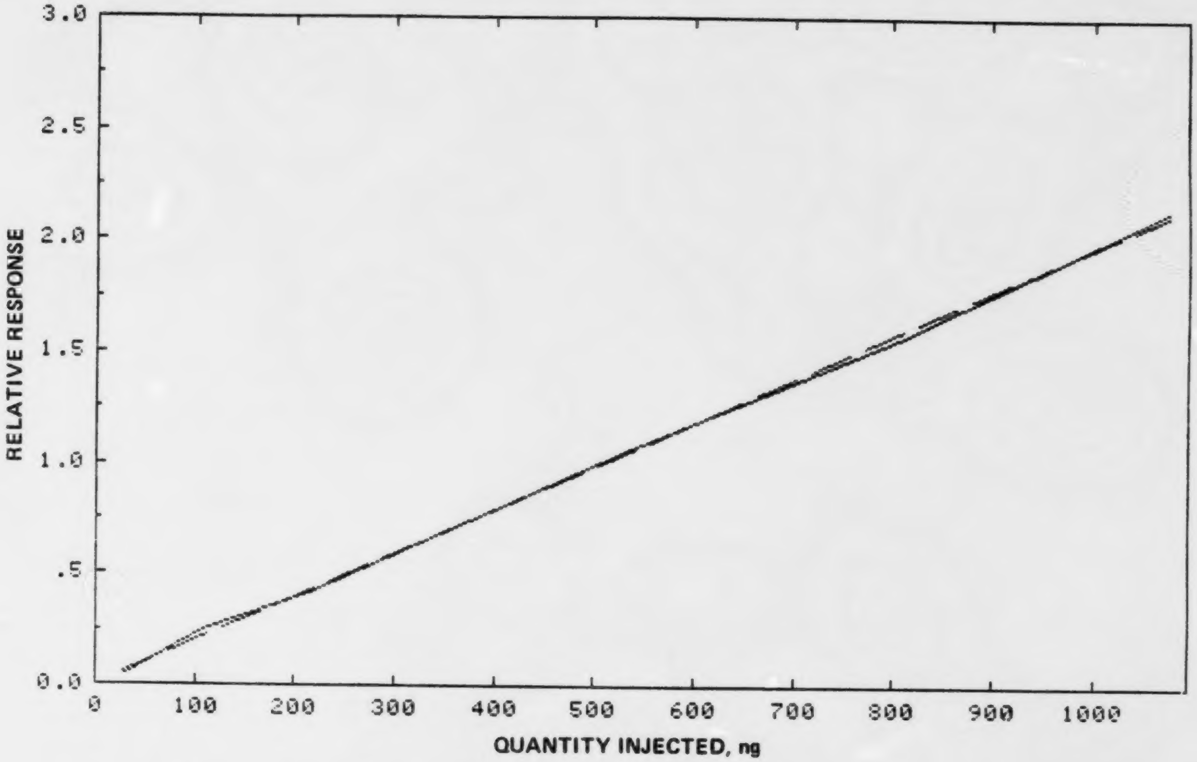

Figure A-46. Calibration curve for the determination of aramite by GC/FID.

Range: 54 - 1100 ng
Correlation coefficient: 0.999
Slope: 2.0×10^{-3}
y-Intercept: 5.4×10^{-3}

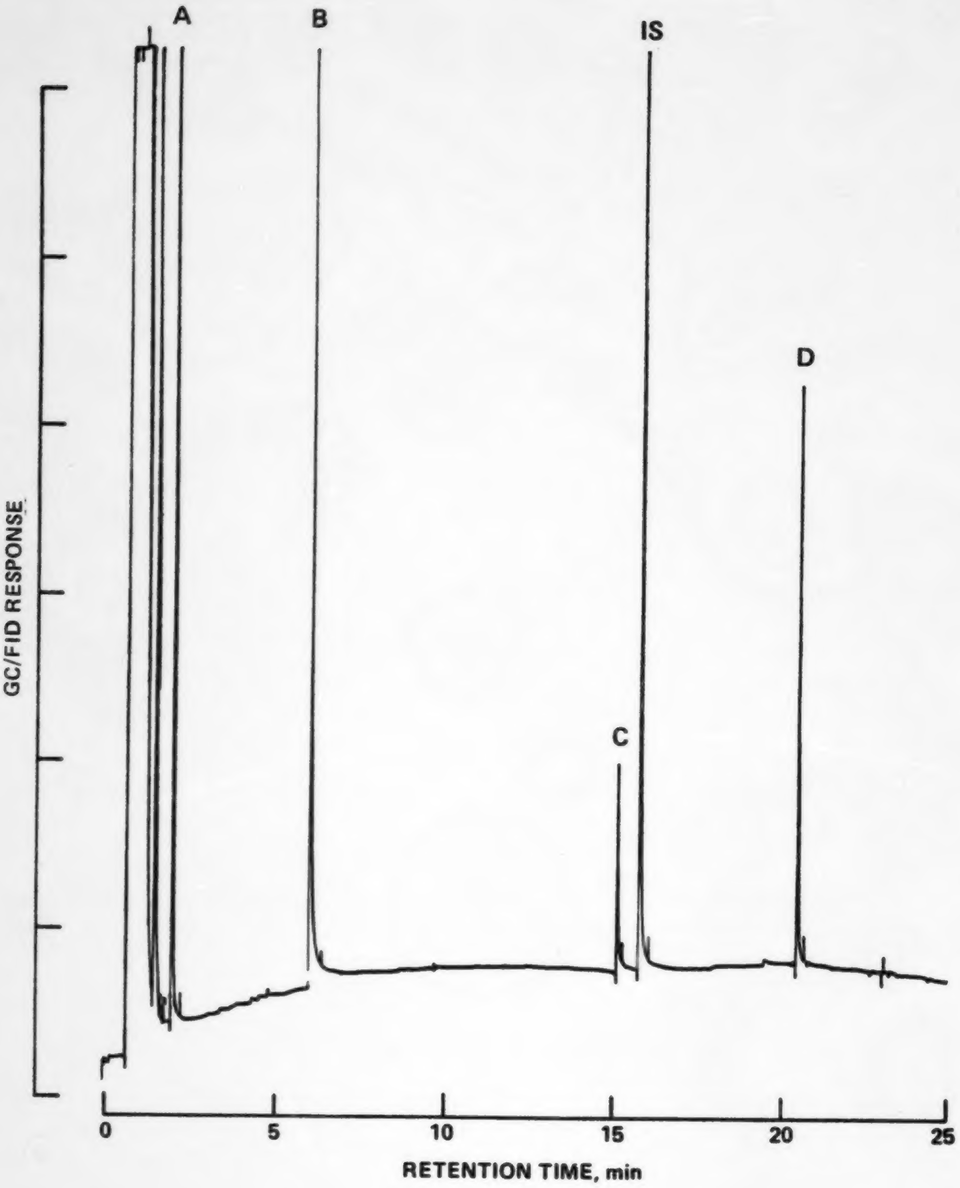

Figure A-47. Chromatogram by GC/FID for

(A) 2-methyllactonitrile(t_R = 2.2 min),
(B) p-cresol(t_R = 6.2 min),
(C) dimethoate(t_R = 15.3 min), and
(D) chlorobenzilate(t_R = 20.6 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

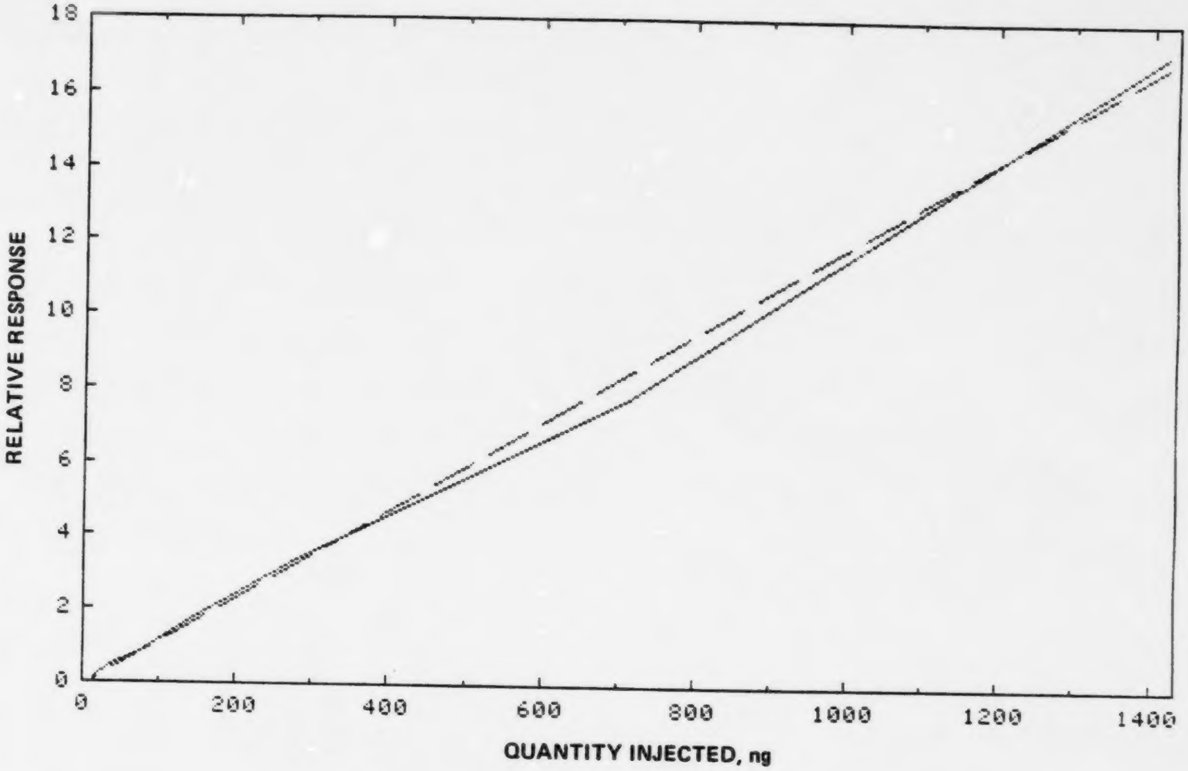

Figure A-48. Calibration curve for the determination of 2-methyllactonitrile by GC/FID.

Range: 71 - 1400 ng
Correlation coefficient: 0.999
Slope: 1.2 x 10^{-2}
y-Intercept: -8.3 x 10^{-2}

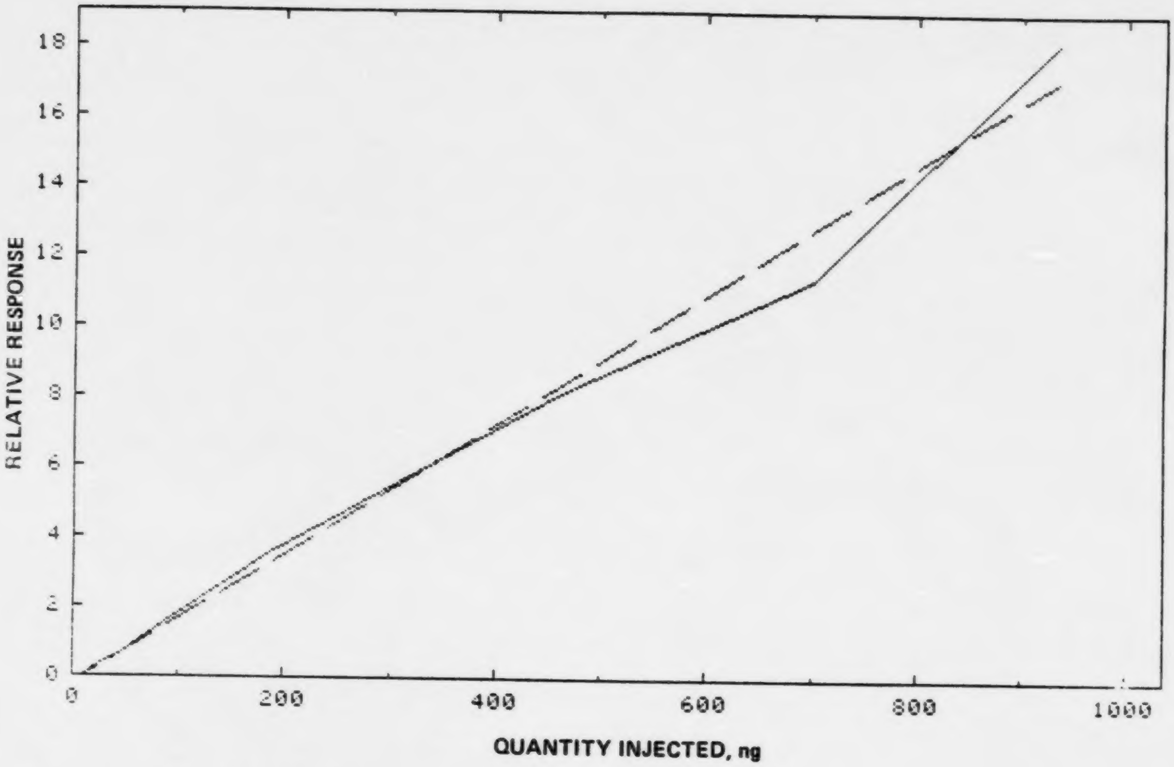

Figure A-49. Calibration curve for the determination of p-cresol by GC/FID.

Range: 47 - 930 ng
Correlation coefficient: 0.995
Slope: 1.8×10^{-2}
y-Intercept: -1.8×10^{-1}

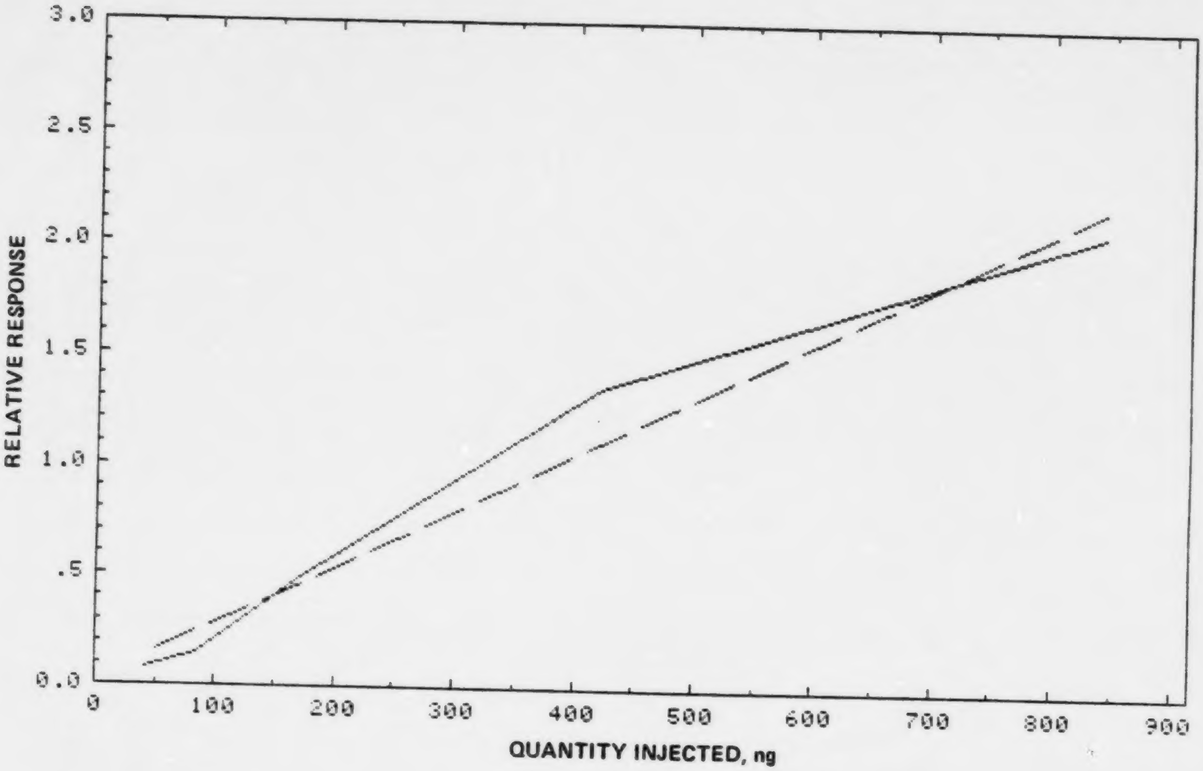

Figure A-50. Calibration curve for the determination of dimethoate by GC/FID.

Range: 84 - 840 ng
Correlation coefficient: 0.985
Slope: 2.6 x 10^{-3}
y-Intercept: 2.9 x 10^{-2}

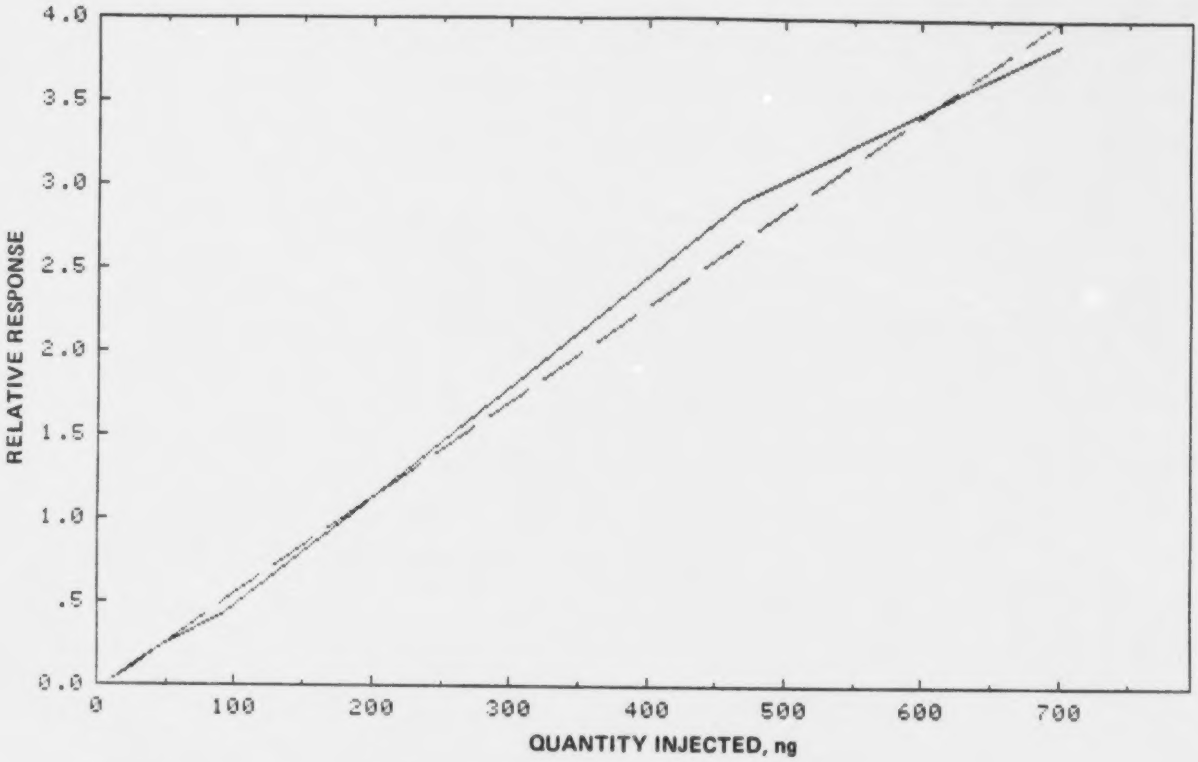

Figure A-51. Calibration curve for the determination of chlorobenzilate by GC/FID.

Range: 23 - 700 ng
Correlation coefficient: 0.997
Slope: 5.8 x 10-3
y-Intercept: -3.0 x 10-2

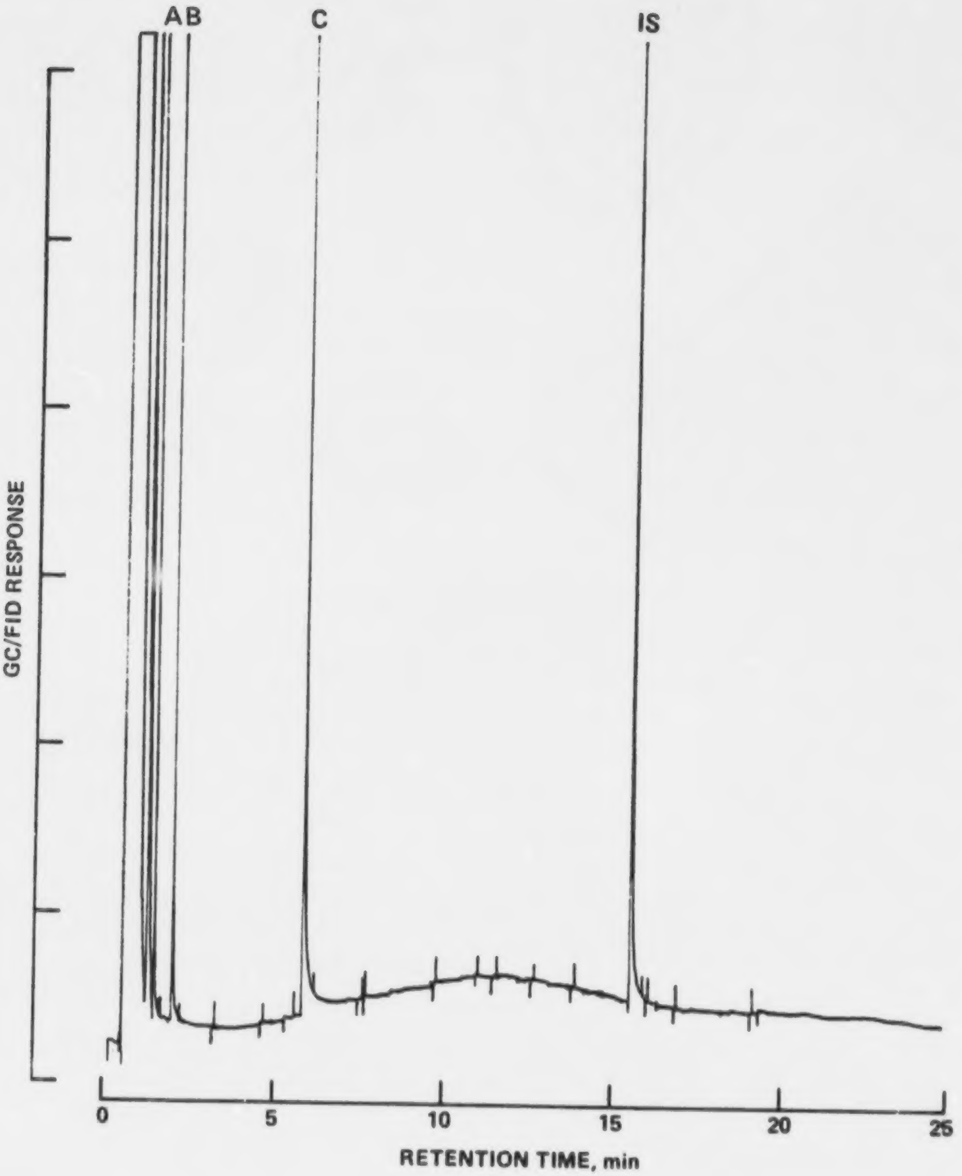

Figure A-52. Chromatogram by GC/FID for

(A) methyl methacrylate(t_R = 1.8 min),
(B) ethyl methacrylate(t_R = 2.3 min), and
(C) m-cresol(t_R = 6.3 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

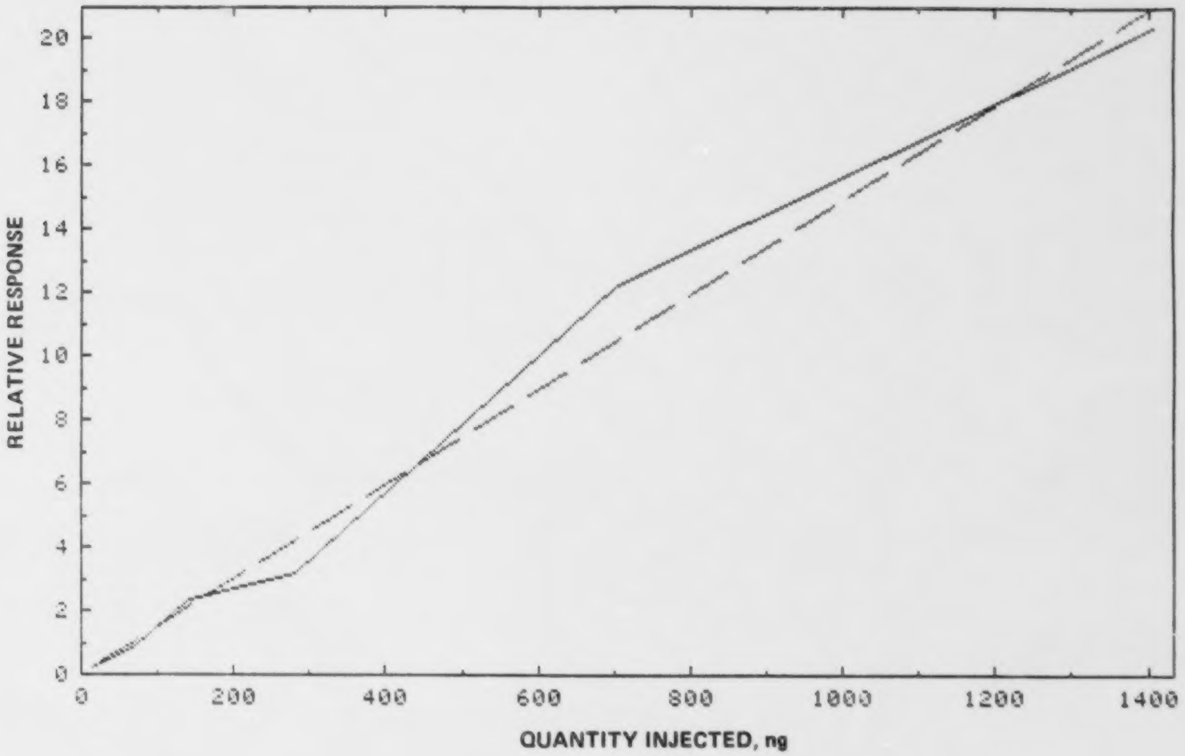

Figure A-53. Calibration curve for the determination of methyl methacrylate by GC/FID.

Range: 14 - 1400 ng
Correlation coefficient: 0.994
Slope: 1.5×10^{-2}
y-Intercept: 1.3×10^{-2}

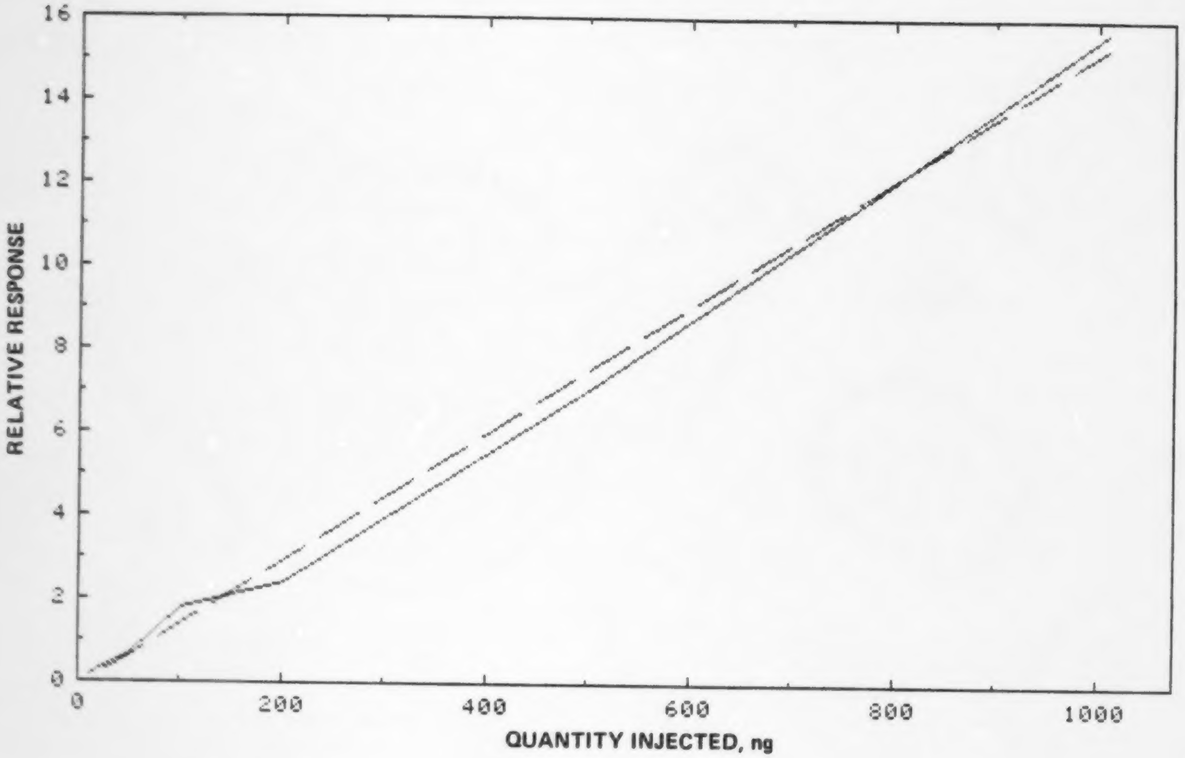

Figure A-54. Calibration curve for the determination of ethyl methacrylate by GC/FID.

Range: 50 - 1000 ng
Correlation coefficient: 0.998
Slope: 1.5 x 10^{-2}
y-Intercept: -1.4 x 10^{-1}

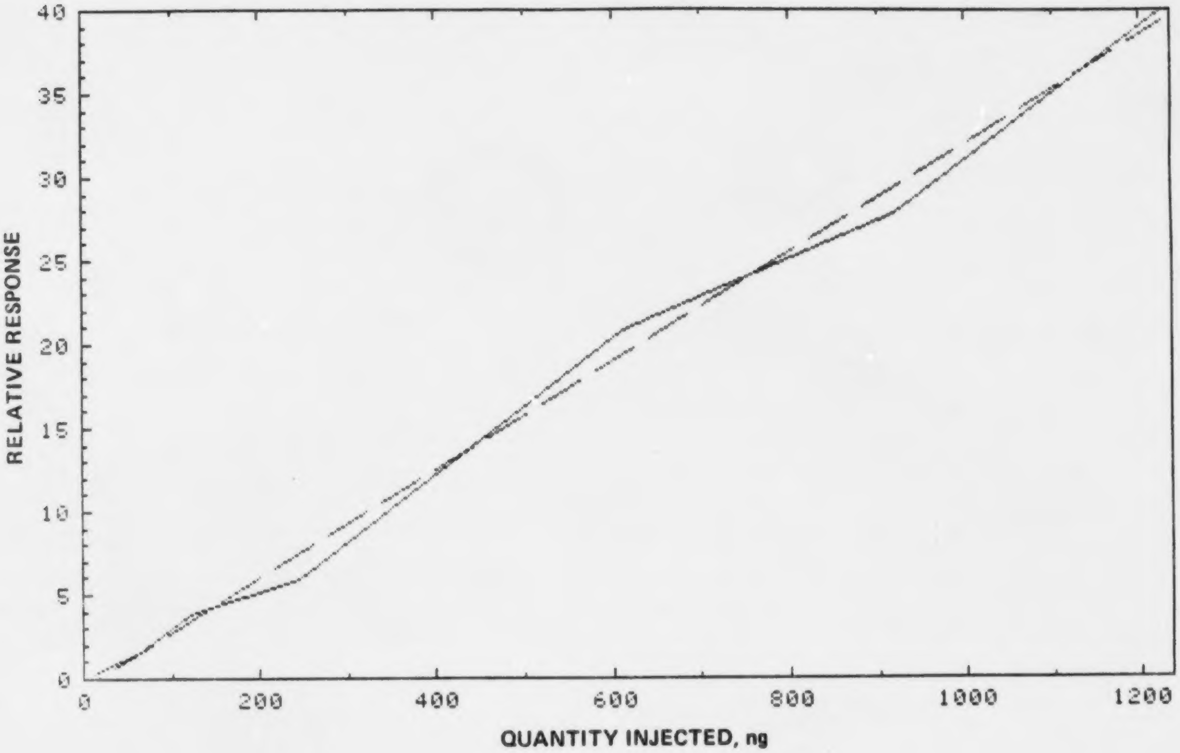

Figure A-55. Calibration curve for the determination of m-cresol by GC/FID.

Range: 61 - 1200 ng
Correlation coefficient: 0.998
Slope: 3.2 x 10^{-2}
y-Intercept: -4.8 x 10^{-1}

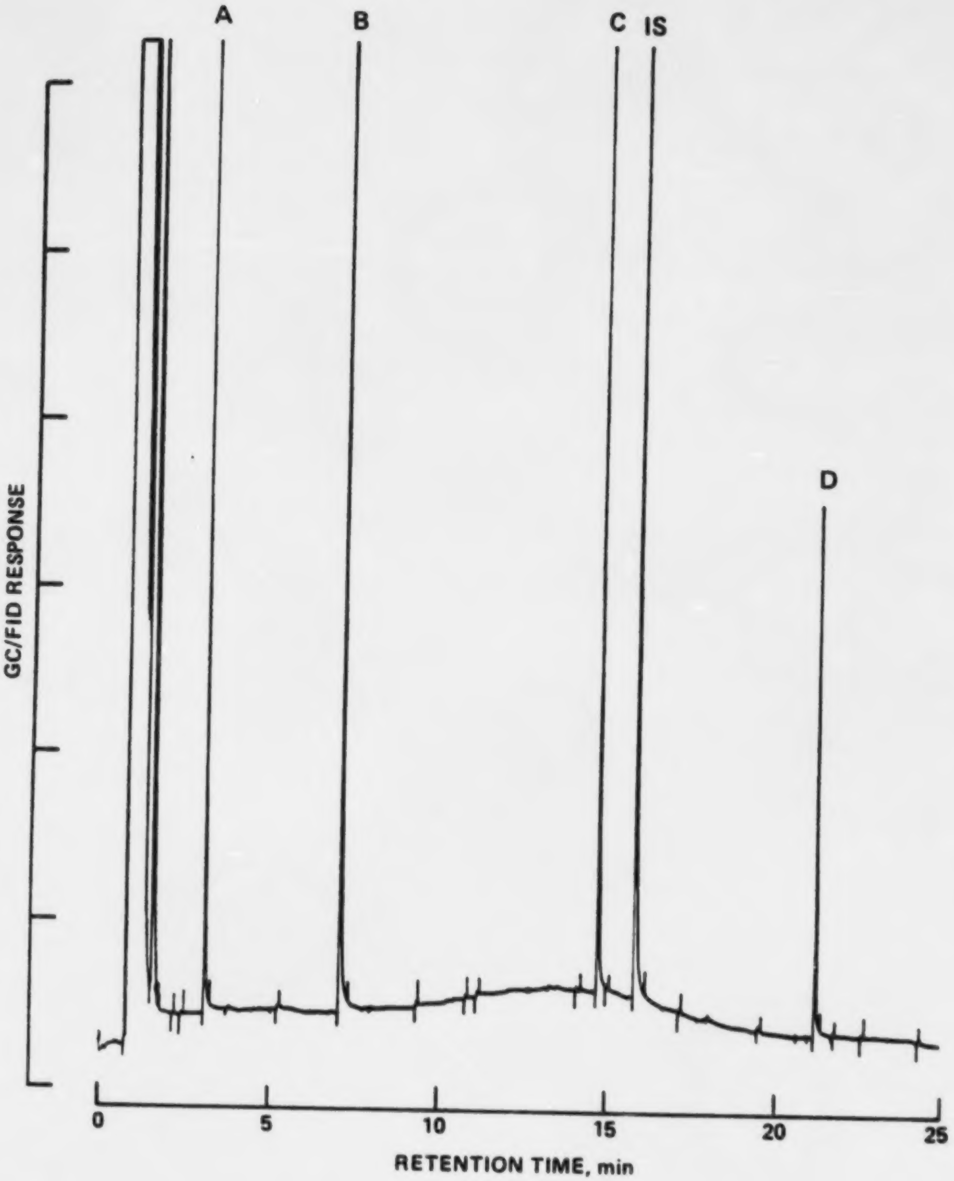

Figure A-56. Chromatogram by GC/FID for

(A) methyl methanesulfonate(t_R = 3.2 min),
(B) (dichloromethyl)benzene(t_R = 7.3 min),
(C) phosphorodithioic acid, O.O-diethyl S-((ethylthio)methyl) ester(t_R = 14.9), and
(D) phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)sulfonyl)phenyl) ester t_R = 21.3 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

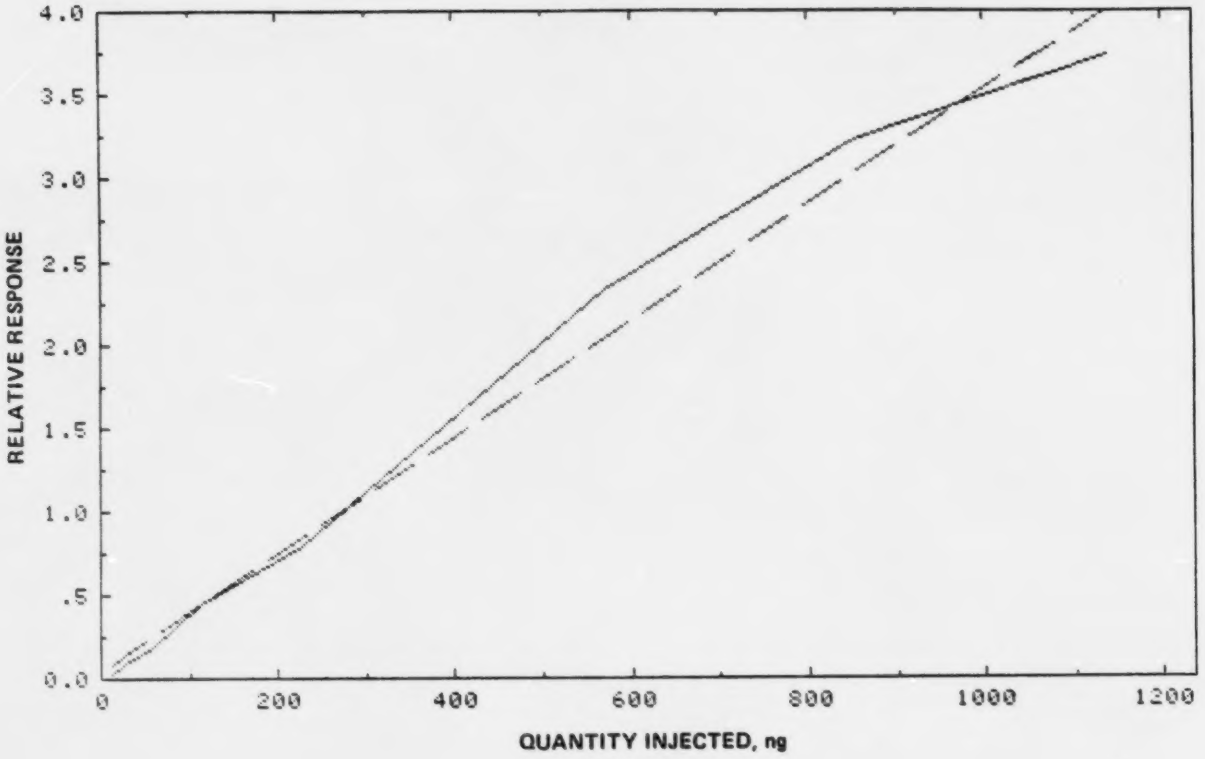

Figure A-57. Calibration curve for the determination of methyl methanesulfonate by GC/FID.

Range: 100 - 1100 ng
Correlation coefficient: 0.993
Slope: 3.5×10^{-3}
y-Intercept: 4.6×10^{-2}

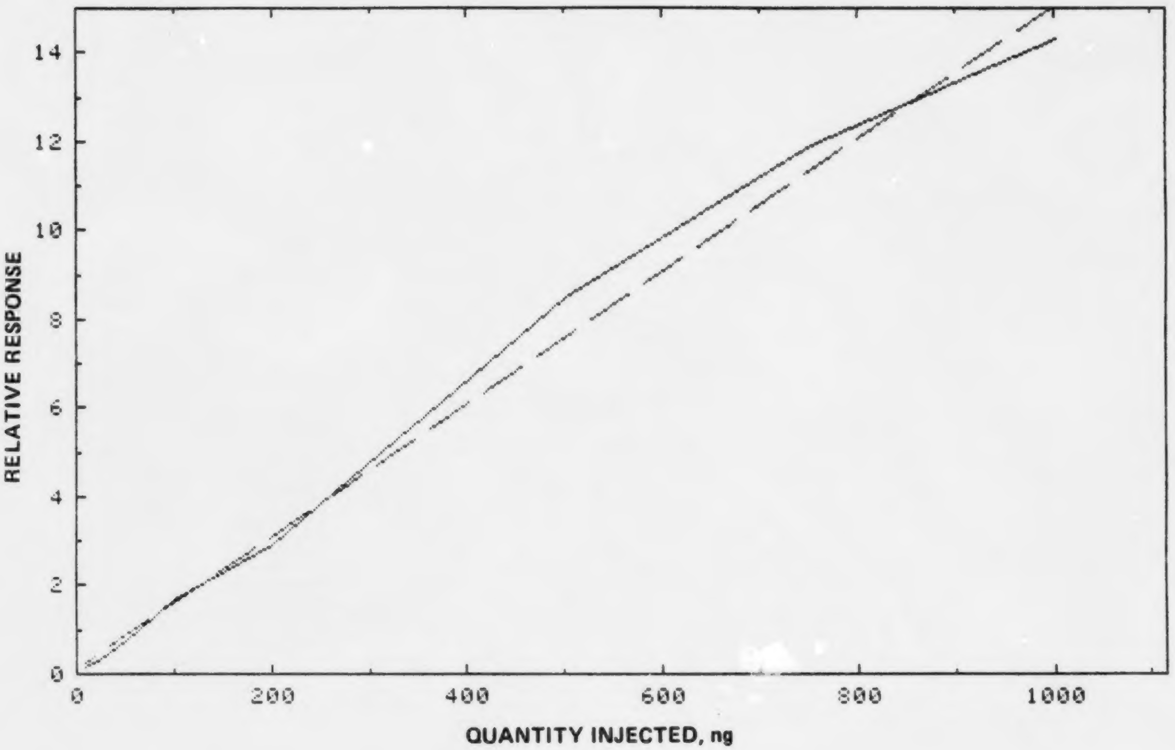

Figure A-58. Calibration curve for the determination of (dichloromethyl)benzene by GC/FID.

Range: 50 - 1000 ng
Correlation coefficient: 0.996
Slope: 1.5×10^{-2}
y-Intercept: 1.2×10^{-1}

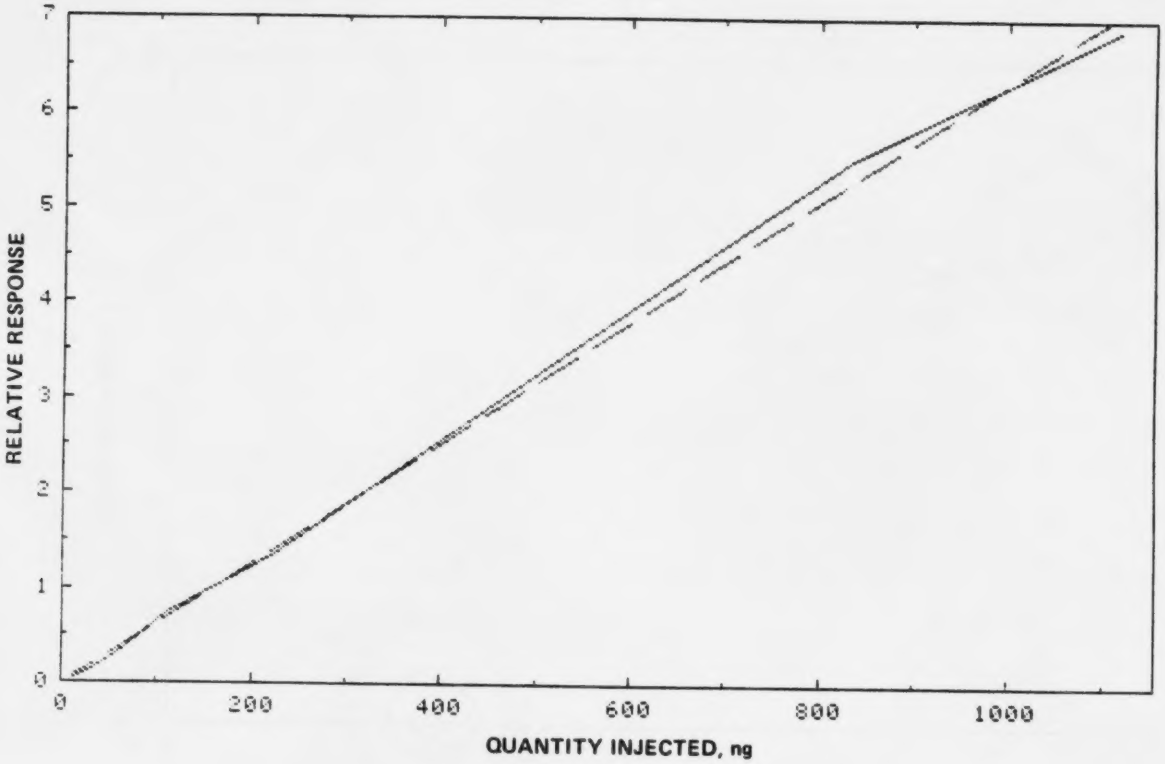

Figure A-59. Calibration curve for the determination of phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester by GC/FID.

Range: 56 - 1100 ng
Correlation coefficient: 0.999
Slope: 6.4×10^{-3}
y-Intercept: 1.0×10^{-2}

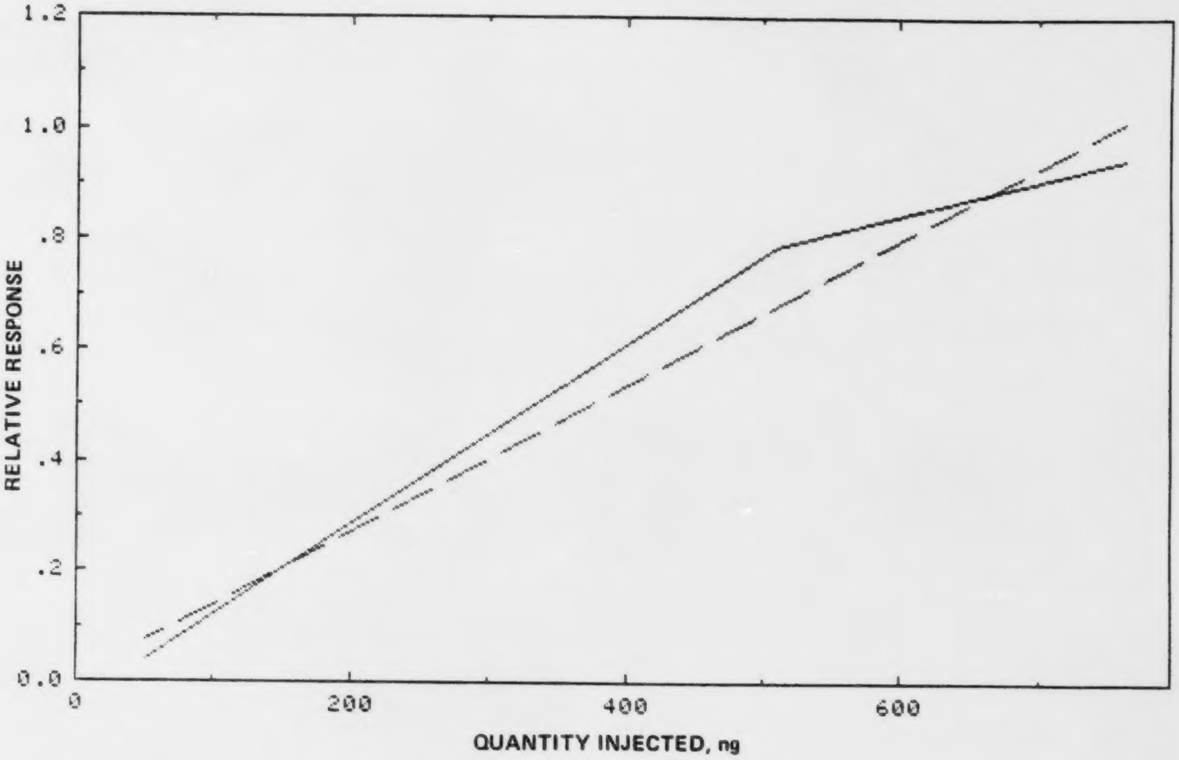

Figure A-60. Calibration curve for the determination of phosphorothioic acid, O,O-dimethyl O-(p-((dimethylamino)sulfonyl)phenyl) ester by GC/FID.

Range: 200 - 760 ng
Correlation coefficient: 0.987
Slope: 1.3×10^{-3}
y-Intercept: 7.6×10^{-3}

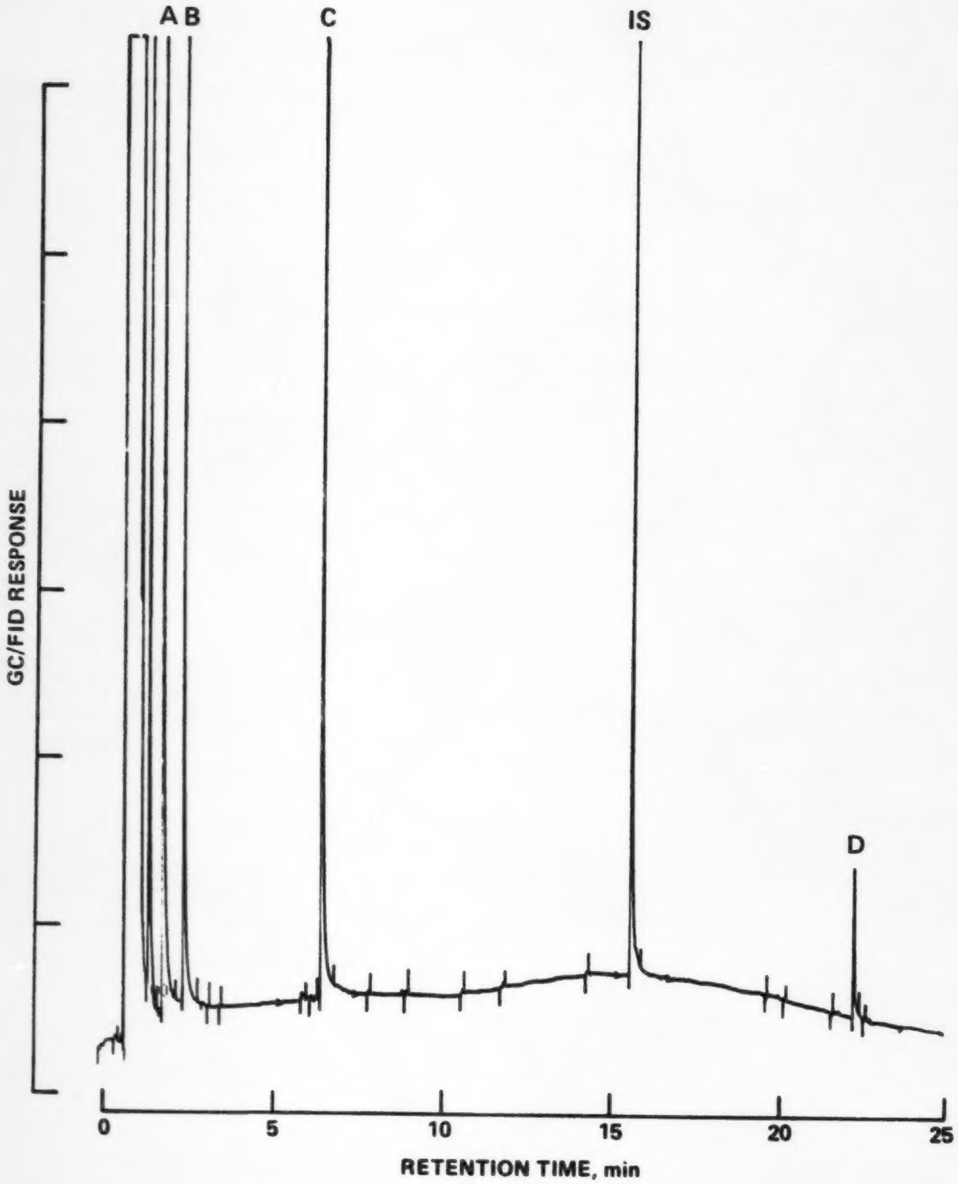

Figure A-61. Chromatogram by GC/FID for

(A) pyridine(t_R = 2.0 min),
(B) 3-chloropropionitrile(t_R = 2.7 min),
(C) α,α-dimethylphenethylamine(t_R = 6.8 min), and
(D) 4,4'-methylenebis(2-chloroaniline)(t_R = 22.6 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

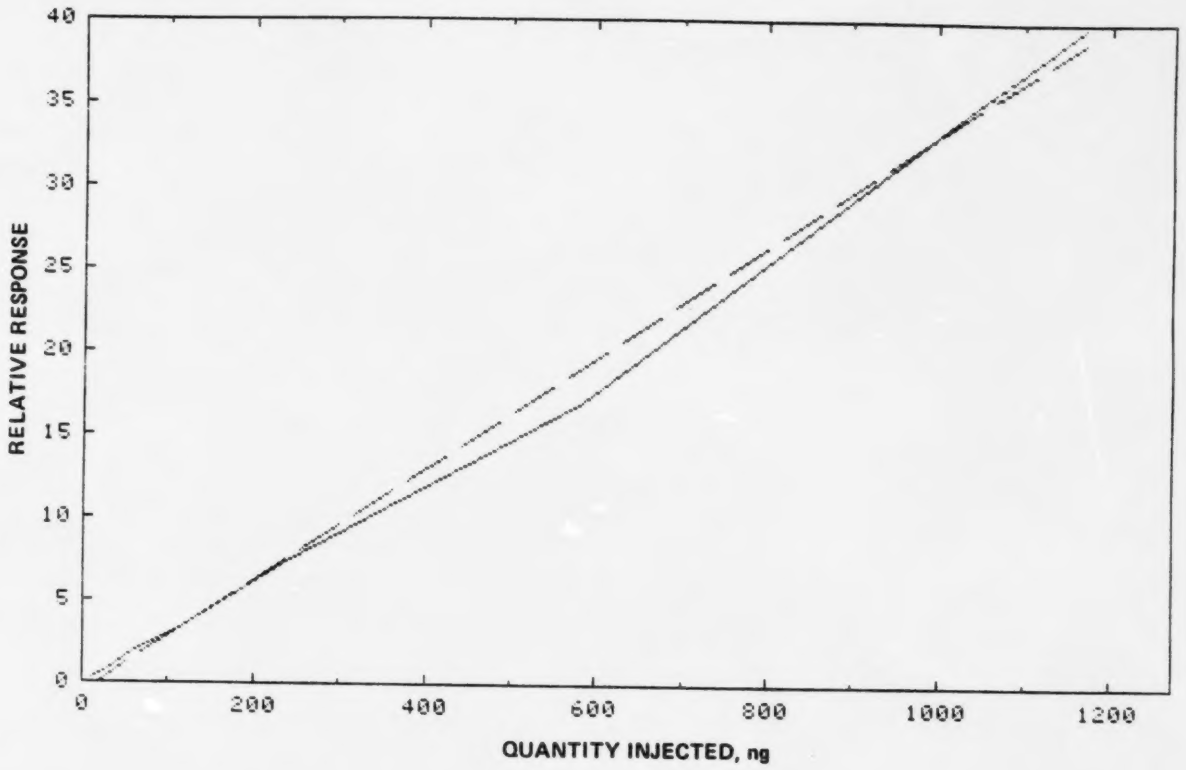

Figure A-62. Calibration curve for the determination of pyridine by GC/FID.

Range: 120 - 1200 ng
Correlation coefficient: 0.998
Slope: 3.4 x 10-2
y-Intercept: -5.2 x 10-1

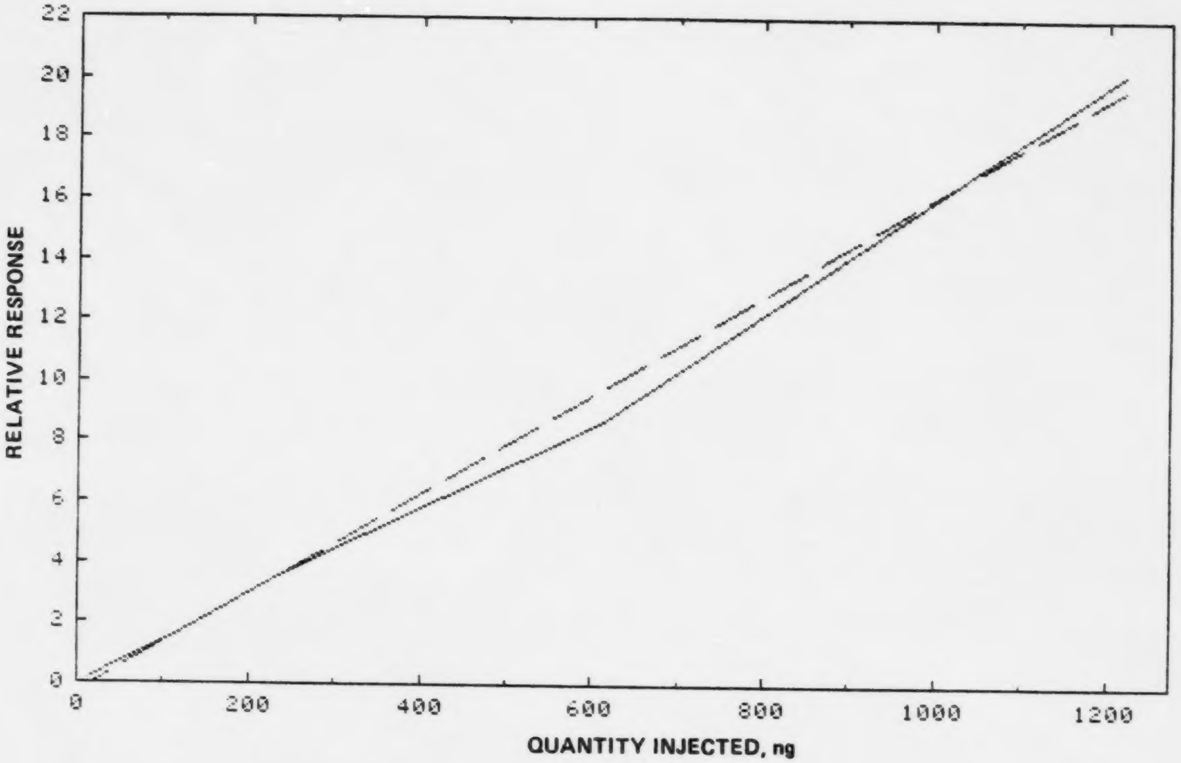

Figure A-63. Calibration curve for the determination of 3-chloropropionitrile by GC/FID.

Range: 120 - 1200 ng
Correlation coefficient: 0.998
Slope: 1.6×10^{-2}
y-Intercept: -2.7×10^{-1}

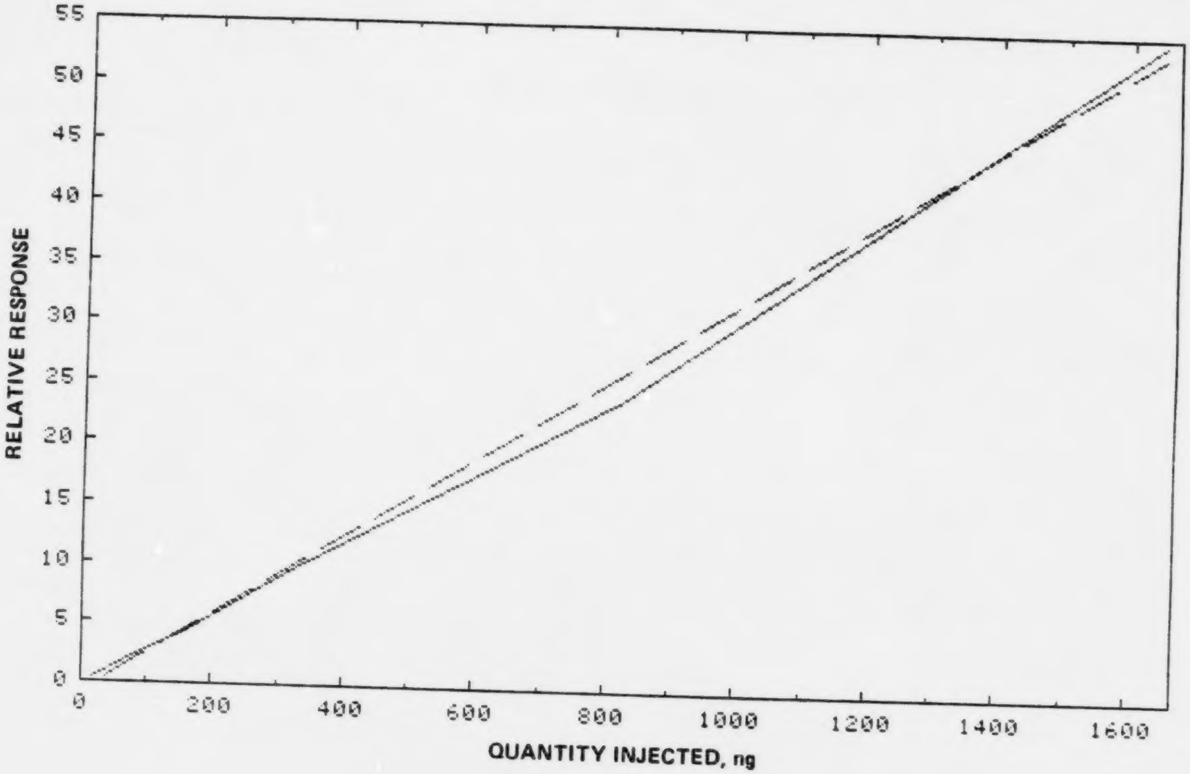

Figure A-64. Calibration curve for the determination of α,α-dimethylphenethylamine by GC/FID.

Range: 160 - 1600 ng
Correlation coefficient: 0.998
Slope: 3.3×10^{-2}
y-Intercept: -7.3×10^{-1}

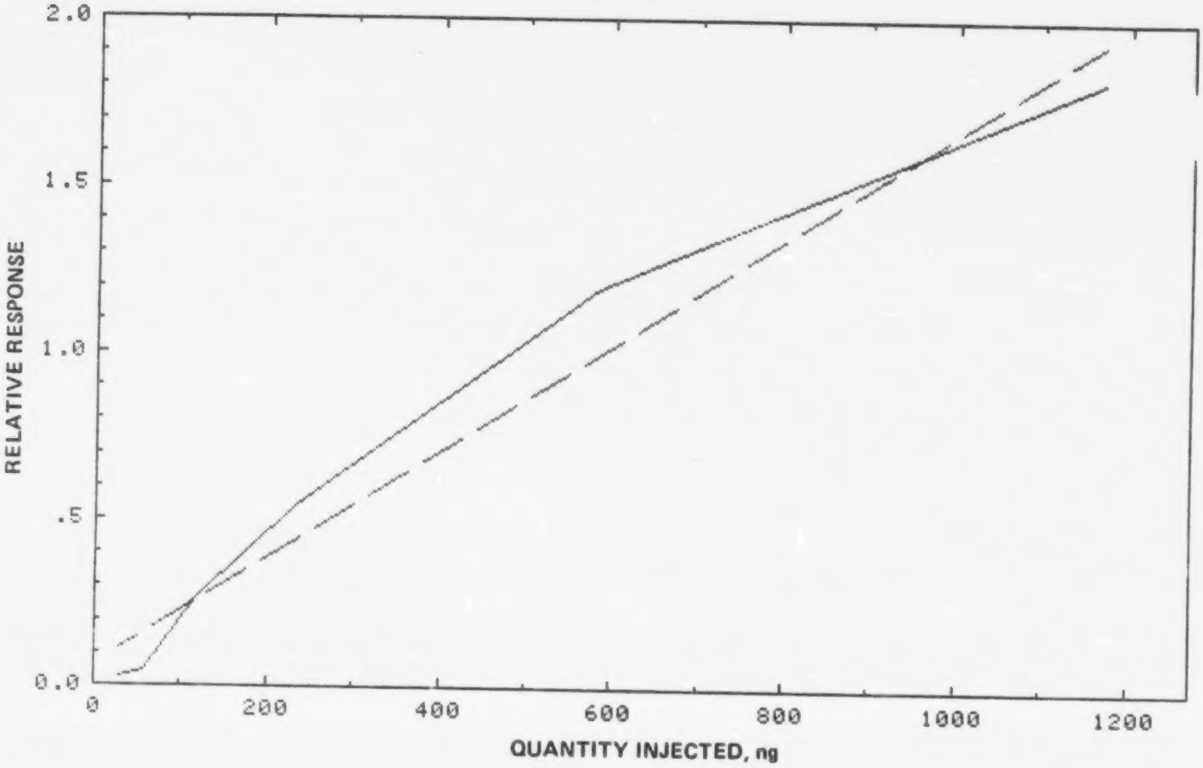

Figure A-65. Calibration curve for the determination of 4,4'-methylenebis(2-chloroaniline) by GC/FID.

Range: 120 - 1200 ng
Correlation coefficient: 0.984
Slope: 1.6 x 10-3
y-Intercept: 6.7 x 10-2

APPENDIX B

CHROMATOGRAMS, MASS SPECTRA, AND CALIBRATION CURVES FOR GC/MS DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference mass spectrum Figure No.	Reference calibration curve Figure No.
Acetophenone	B-1	B-2	B-3
4-Aminobiphenyl	B-1	B-6	B-7
Aniline	B-10	B-11	B-12
Aramite	B-77	B-80	B-81
Benzenethiol	B-17	B-18	B-19
Butylbenzyl phthalate	B-54	B-61	B-62
Chlorobenzilate	B-82	B-89	B-90
p-Chloro-*m*-cresol	B-35	B-38	B-39
2-Chlorophenol	B-24	B-25	B-26
3-Chloropropionitrile	B-107	B-110	B-111
m-Cresol	B-91	B-96	B-97
o-Cresol	B-35	B-36	B-37
p-Cresol	B-82	B-85	B-86
Diallate	B-44	B-45	B-46
Dibutyl phthalate	B-35	B-42	B-43
(Dichloromethyl)benzene	B-98	B-101	B-102
Diethyl phthalate	B-54	B-57	B-58
Diisobutyl phthalate	B-54	B-59	B-60
Dimethoate	B-82	B-87	B-88
p-Dimethylaminoazobenzene	B-10	B-15	B-16
α,α-Dimethylphenethylamine	B-107	B-112	B-113
2,4-Dimethylphenol	B-49	B-50	B-51
dimethyl phthalate	B-54	B-55	B-56
4,6-Dinitro-*o*-cresol	B-35	B-40	B-41
Dioctyl phthalate	B-54	B-63	B-64
Diphenylamine	B-65	B-66	B-67
Disulfoton	B-44	B-47	B-48
Ethyl carbamate	B-68	B-69	B-70
Ethyl methacrylate	B-91	B-94	B-95
Isosafrole	B-77	B-78	B-79
Kepone	B-1	B-8	B-9
Methoxychlor	B-24	B-33	B-34
4,4'-Methylenebis-(2-chloroaniline)	B-107	B-114	B-115

(continued)

APPENDIX B

CHROMATOGRAMS, MASS SPECTRA, AND CALIBRATION CURVES FOR GC/MS DETERMINATIONS

Index

(continued)

Compound	Reference chromatogram Figure No.	Reference mass spectrum Figure No.	Reference calibration curve Figure No.
2-Methyllactonitrile	B-82	B-83	B-84
Methyl methacrylate	B-91	B-92	B-93
Methyl methanesulfonate	B-98	B-99	B-100
Methyl parathion	B-17	B-22	B-23
2-Naphthylamine	B-68	B-75	B-76
Octamethyl pyrophosphoramide	B-17	B-20	B-21
Pentachloronitrobenzene	B-24	B-31	B-32
Pentachlorophenol	B-24	B-29	B-30
m-Phenylenediamine	B-68	B-73	B-74
o-Phenylenediamine	B-68	B-71	B-72
p-Phenylenediamine	B-1	B-4	B-5
Phosphorodithioic acid ester[a]	B-98	B-103	B-104
Phosphorothioic acid ester[b]	B-98	B-105	B-106
Pyridine	B-107	B-108	B-109
2,3,4,6-Tetrachlorophenol	B-24	B-27	B-28
2,4,6-Trichlorophenol	B-49	B-52	B-53
O,*O*,*O*-triethyl phosphorothioate	B-10	B-13	B-14

[a] Phosphorodithioic acid, *O*,*O*-diethyl *S*-((ethylthio)methyl) ester.

[b] Phosphorothioic acid, *O*,*O*-dimethyl *O*-(*p*-((dimethylamino)sulfonyl) phenyl) ester.

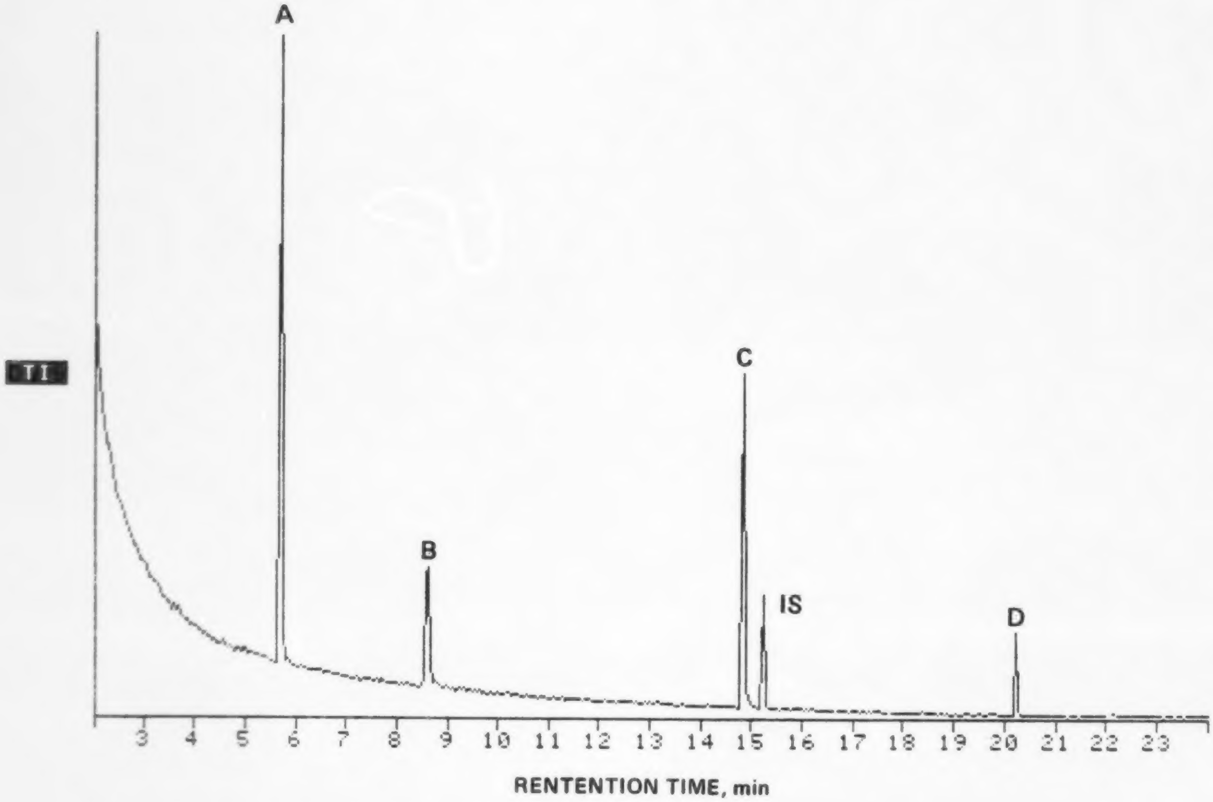

Figure B-1. Chromatogram by GC/MS for

(A) acetophenone(t_R = 5.6 min),
(B) p-phenylenediamine(t_R = 8.7 min),
(C) 4-aminobiphenyl(t_R = 14.9 min), and
(D) kepone(t_R = 20.3 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

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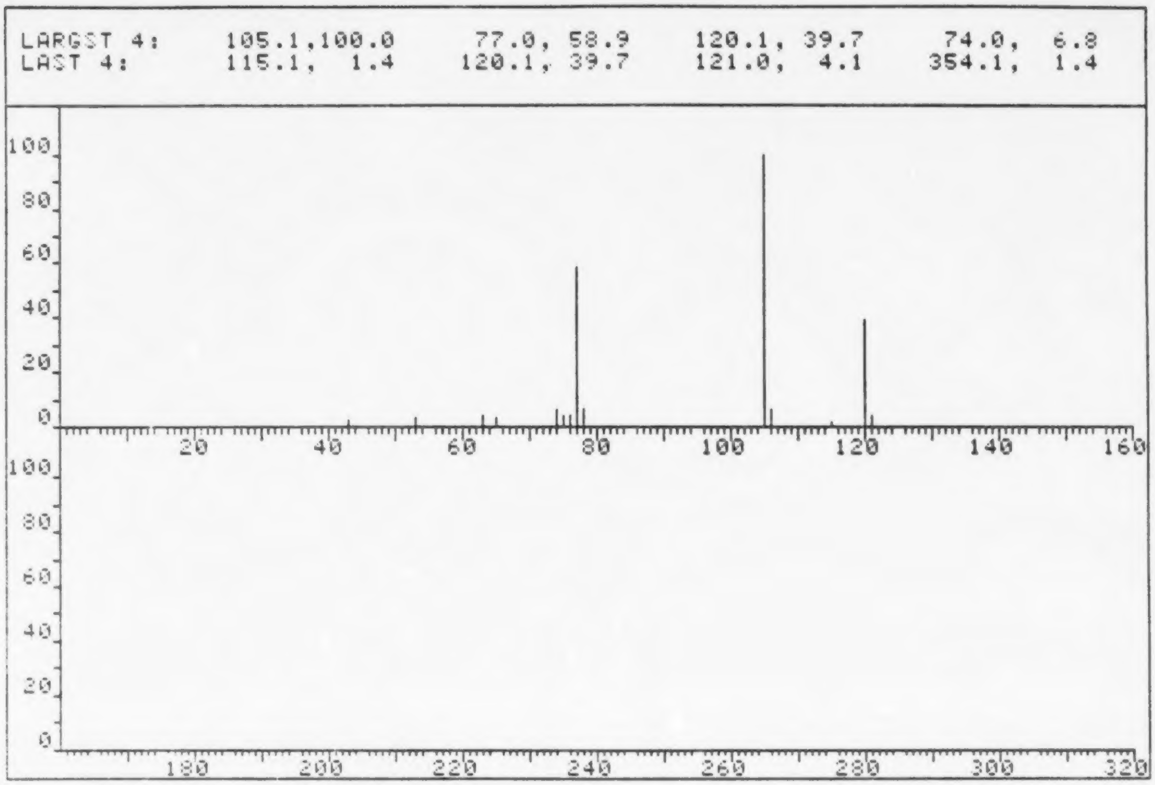


```
LARGST 4:     105.1,100.0      77.0, 58.9     120.1, 39.7      74.0,  6.8
LAST 4:       115.1,   1.4    120.1, 39.7     121.0,  4.1     354.1,  1.4
```

Figure B-2. Mass spectrum for acetophenone.

TABLE B-1. KEY IONS AND RELATIVE ABUNDANCES FOR ACETOPHENONE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.0	2.1	75.1	4.1	106.1	6.2
53.2	3.4	76.0	4.1	115.1	1.4
63.1	4.1	77.0	58.9	120.1	39.7
65.1	3.4	78.0	6.2	121.0	4.1
74.0	6.8	105.1	100.0	354.1	1.4

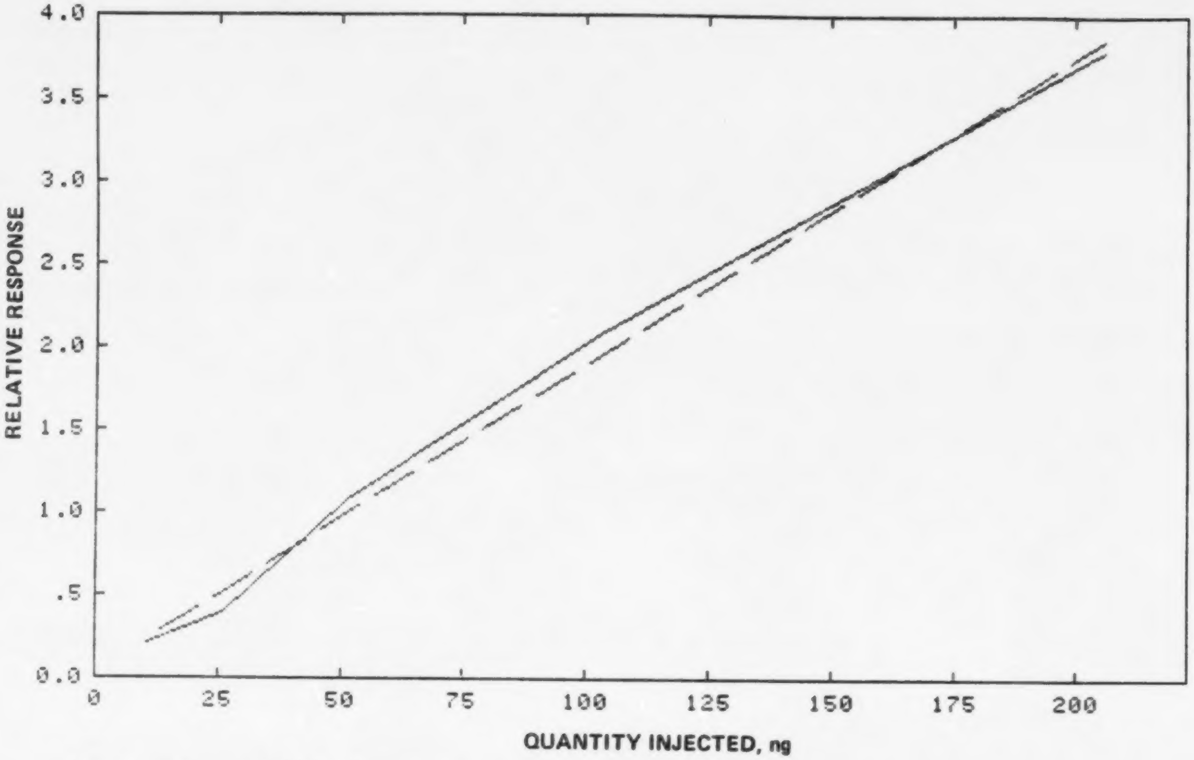
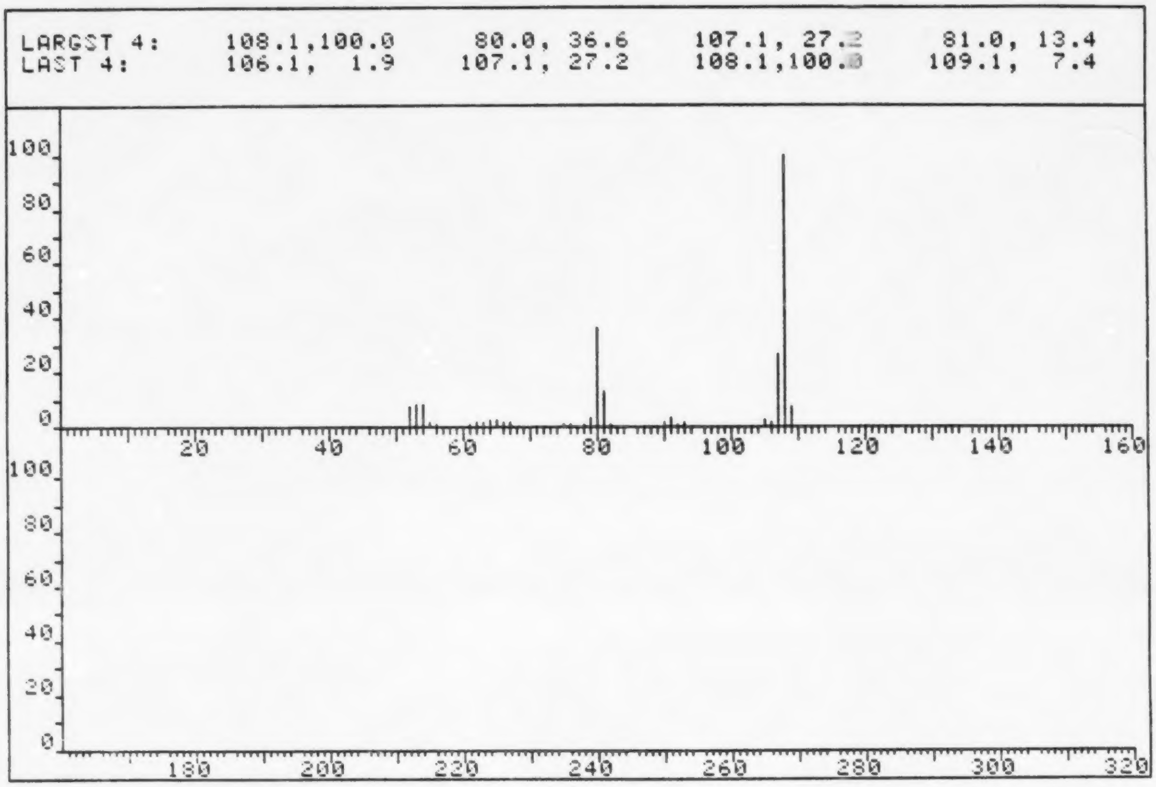


Figure B-3. Calibration curve for the determination of acetophenone by GC/MS.

Range: 10 - 210 ng
Correlation coefficient: 0.997
Slope: 1.8×10^{-2}
y-Intercept: 4.0×10^{-2}



```
LARGST 4:     108.1,100.0     80.0, 36.6     107.1, 27.2     81.0, 13.4
LAST 4:       106.1,   1.9   107.1, 27.2     108.1,100.0    109.1,  7.4
```

Figure B-4. Mass spectrum for p-phenylenediamine.

TABLE B-2. KEY IONS AND RELATIVE ABUNDANCES FOR *p*-PHENYLENEDIAMINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
52.1	6.9	66.0	1.3	90.1	1.8
53.1	8.7	67.0	1.9	91.1	2.8
54.0	8.4	74.9	.7	92.1	.9
55.1	1.8	75.9	.9	93.1	1.3
55.9	.9	78.1	1.0	105.1	2.1
61.2	.7	79.0	3.1	106.1	1.9
62.1	1.3	80.0	36.6	107.1	27.2
63.0	1.8	81.0	13.4	108.1	100.0
64.1	2.5	82.1	.7	109.1	7.4
65.0	2.4				

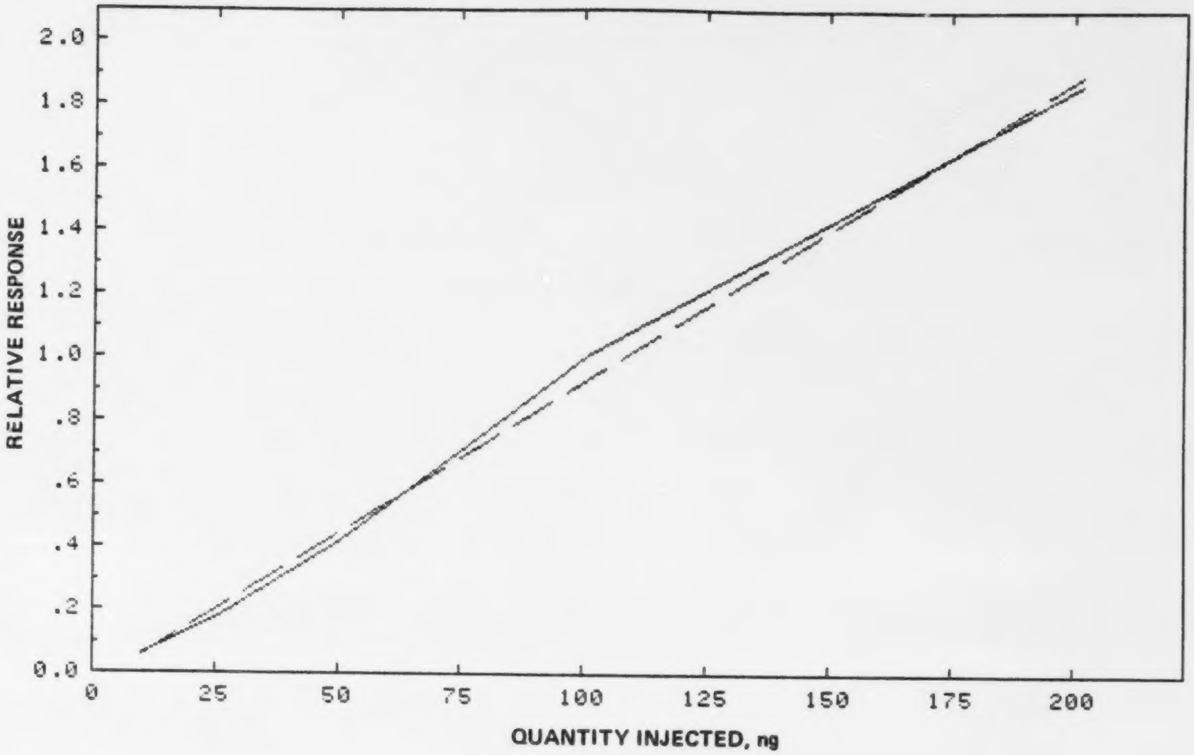
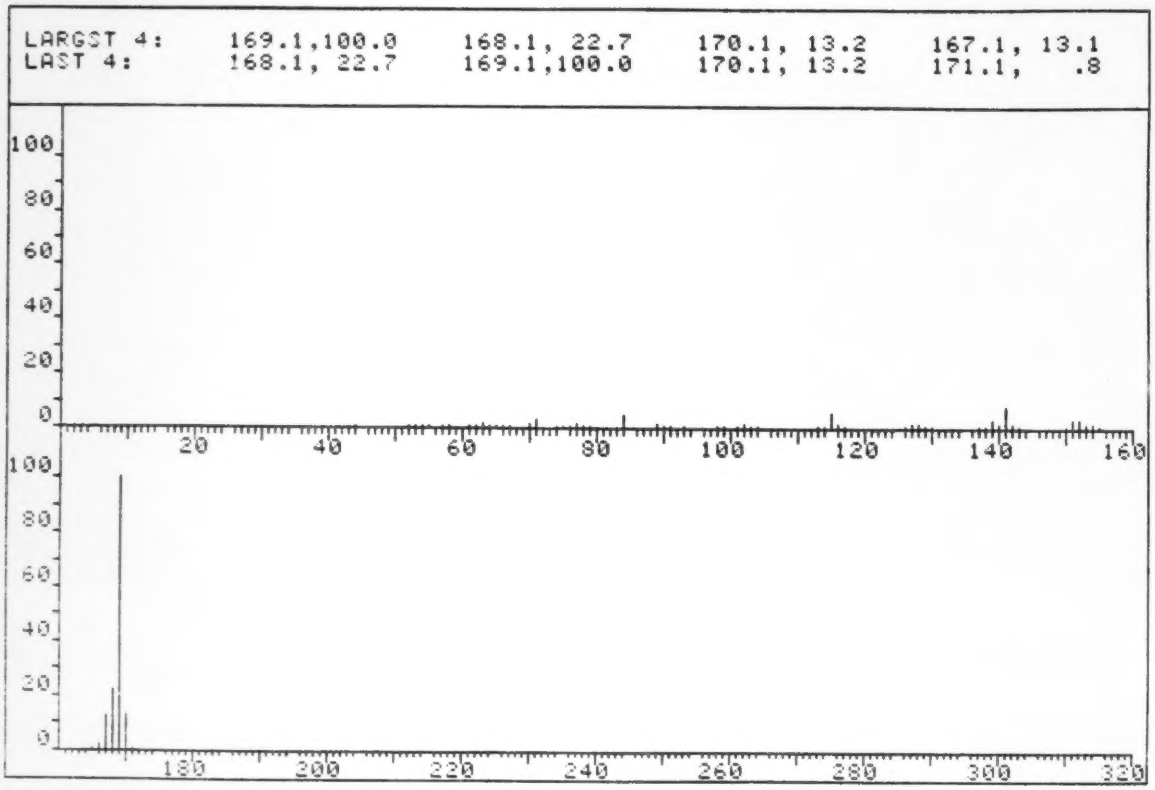


Figure B-5. Calibration curve for the determination of p-phenylenediamine by GC/MS.

Range: 10 - 200 ng
Correlation coefficient: 0.998
Slope: 9.6 x 10^{-3}
y-Intercept: -3.9 x 10^{-2}



```
LARGST 4:     169.1,100.0      168.1, 22.7      170.1, 13.2      167.1, 13.1
LAST 4:       168.1, 22.7      169.1,100.0      170.1, 13.2      171.1,    .8
```

Figure B-6. Mass spectrum for 4-aminobiphenyl.

TABLE B-3. KEY IONS AND RELATIVE ABUNDANCES FOR 4-AMINOBIPHENYL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
44.1	.1	78.1	.4	130.1	.7
52.1	.4	79.0	.3	137.1	.3
53.2	.3	84.5	5.3	138.1	.4
54.0	.5	89.1	1.6	139.0	3.6
54.8	.3	90.1	.6	140.0	2.0
56.8	.3	91.1	.7	141.1	8.1
57.4	.7	93.1	.6	142.0	1.9
58.5	.9	98.0	.4	143.1	1.2
61.1	.4	99.1	.3	150.2	.9
62.0	.7	101.1	.4	151.1	3.4
63.1	1.9	102.1	1.4	152.1	3.2
64.1	.8	103.1	.6	153.1	1.6
65.1	1.3	104.1	.3	154.1	1.9
66.0	.6	113.1	.8	155.1	.3
66.9	.4	114.0	.9	165.2	.3
69.7	.5	115.1	6.0	166.1	2.4
70.5	2.0	116.1	1.5	167.1	13.1
71.5	2.8	117.1	.7	168.1	22.7
74.0	.9	126.1	.7	169.1	100.0
75.0	.9	127.0	1.3	170.1	13.2
76.1	1.0	128.1	1.9	171.1	.8
77.0	2.0	129.2	.4		

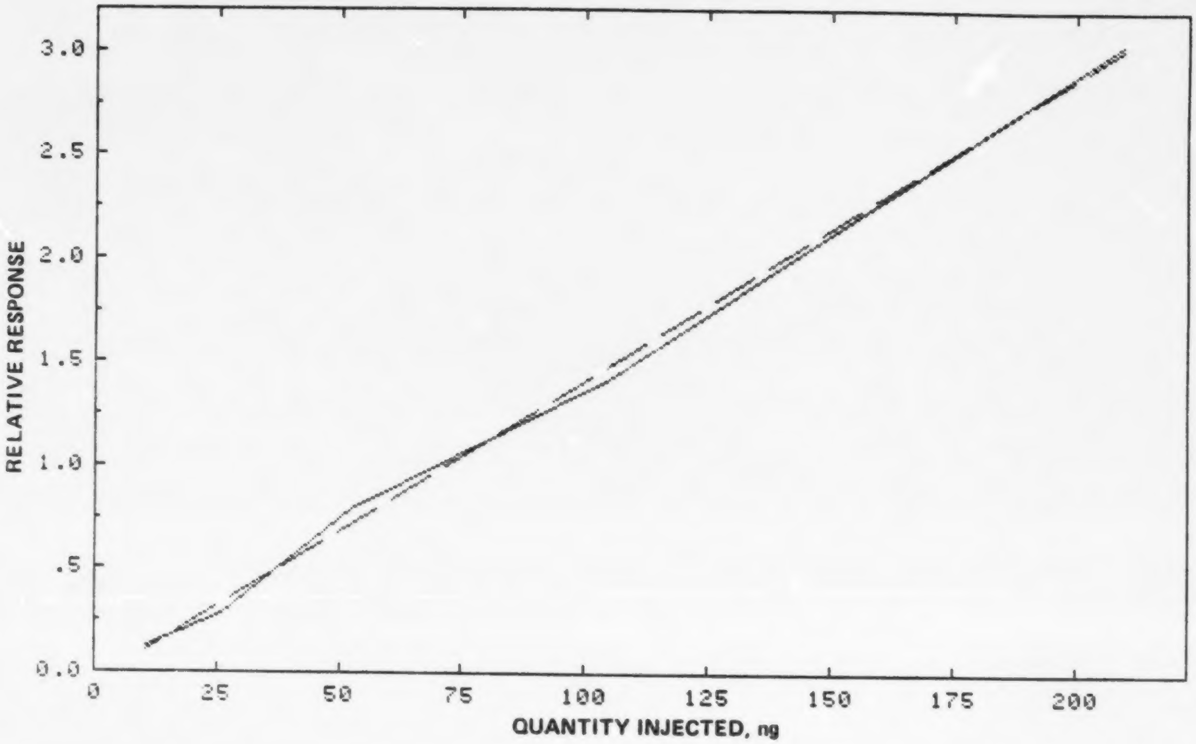
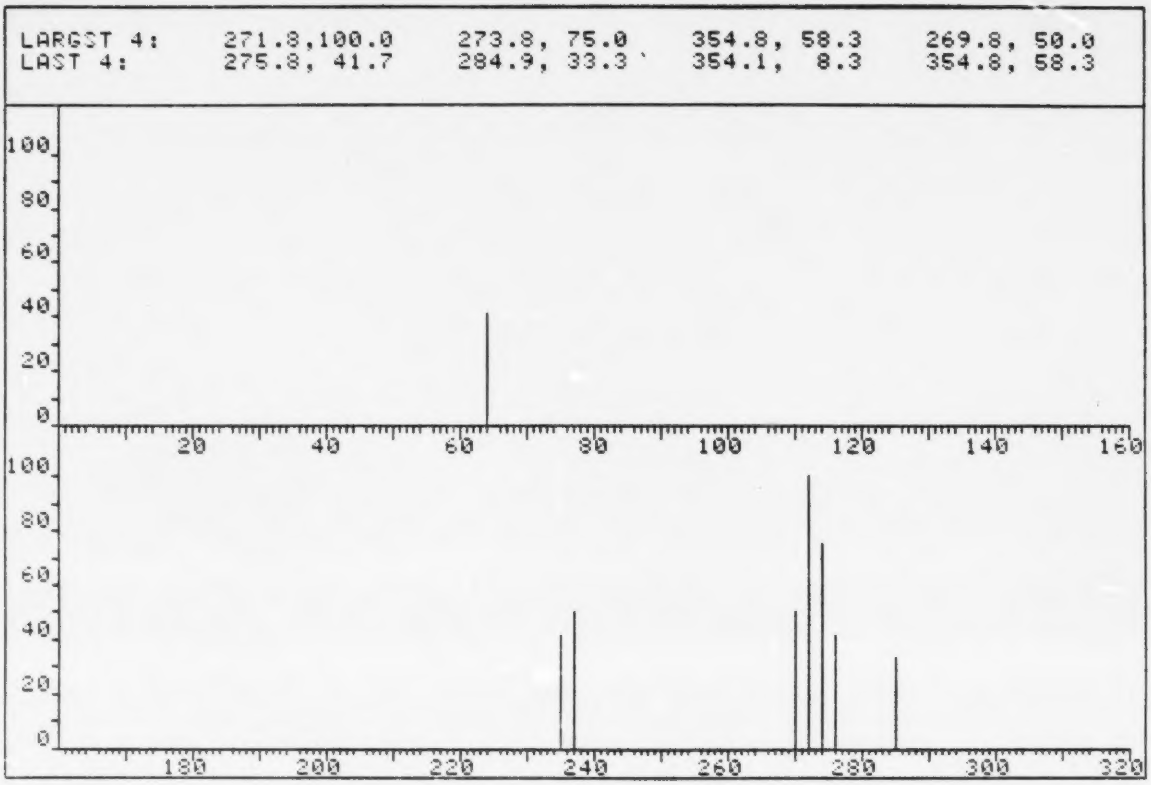


Figure B-7. Calibration curve for the determination of 4-aminobiphenyl by GC/MS.

Range: 26 - 210 ng
Correlation coefficient: 0.999
Slope: 1.5×10^{-2}
y-Intercept: -4.8×10^{-2}



```
LARGST 4:     271.8,100.0     273.8, 75.0     354.8, 58.3     269.8, 50.0
LAST 4:       275.8, 41.7     284.9, 33.3 `   354.1,  8.3     354.8, 58.3
```

Figure B-8. Mass spectrum for kepone.

TABLE B-4. KEY IONS AND RELATIVE ABUNDANCES FOR KEPONE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
64.1	41.7	271.8	100.0	284.9	33.3
234.9	41.7	273.8	75.0	354.1	8.3
237.0	50.0	275.8	41.7	354.8	58.3
269.8	50.0				

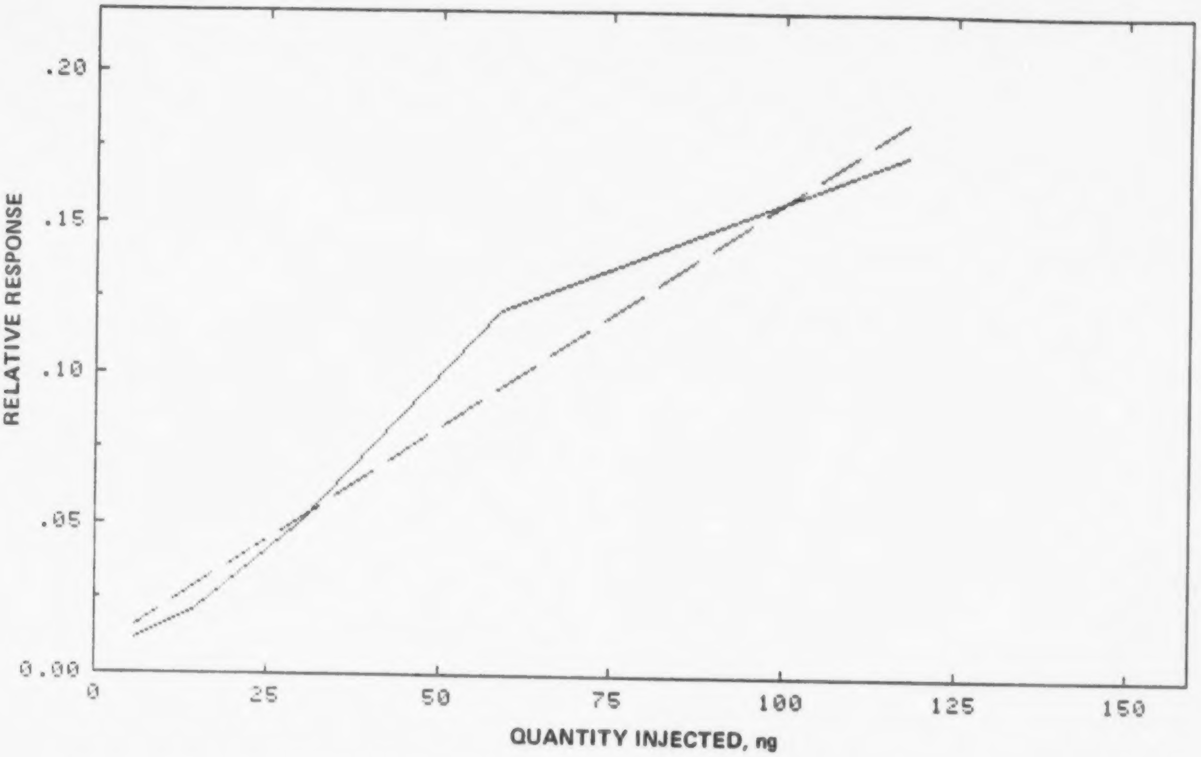


Figure B-9. Calibration curve for the determination of kepone by GC/MS.

Range: 30 - 120 ng
Correlation coefficient: 0.978
Slope: 1.5×10^{-3}
y-Intercept: 7.4×10^{-3}

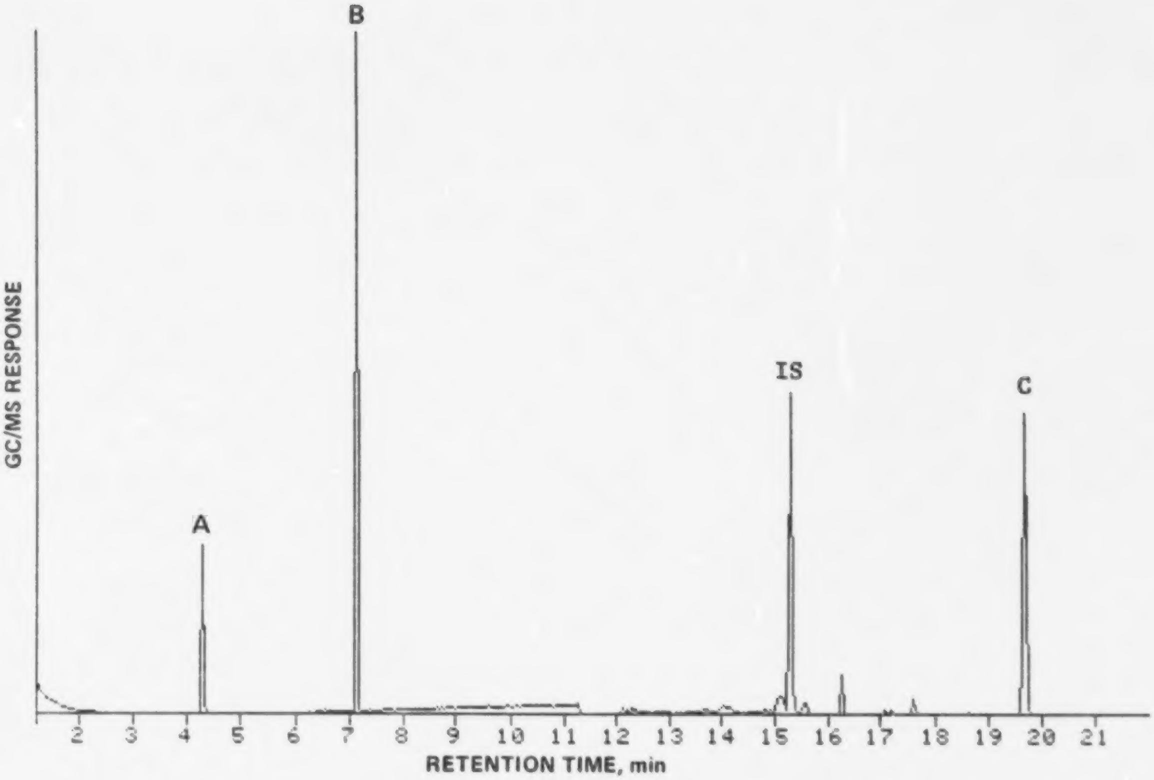
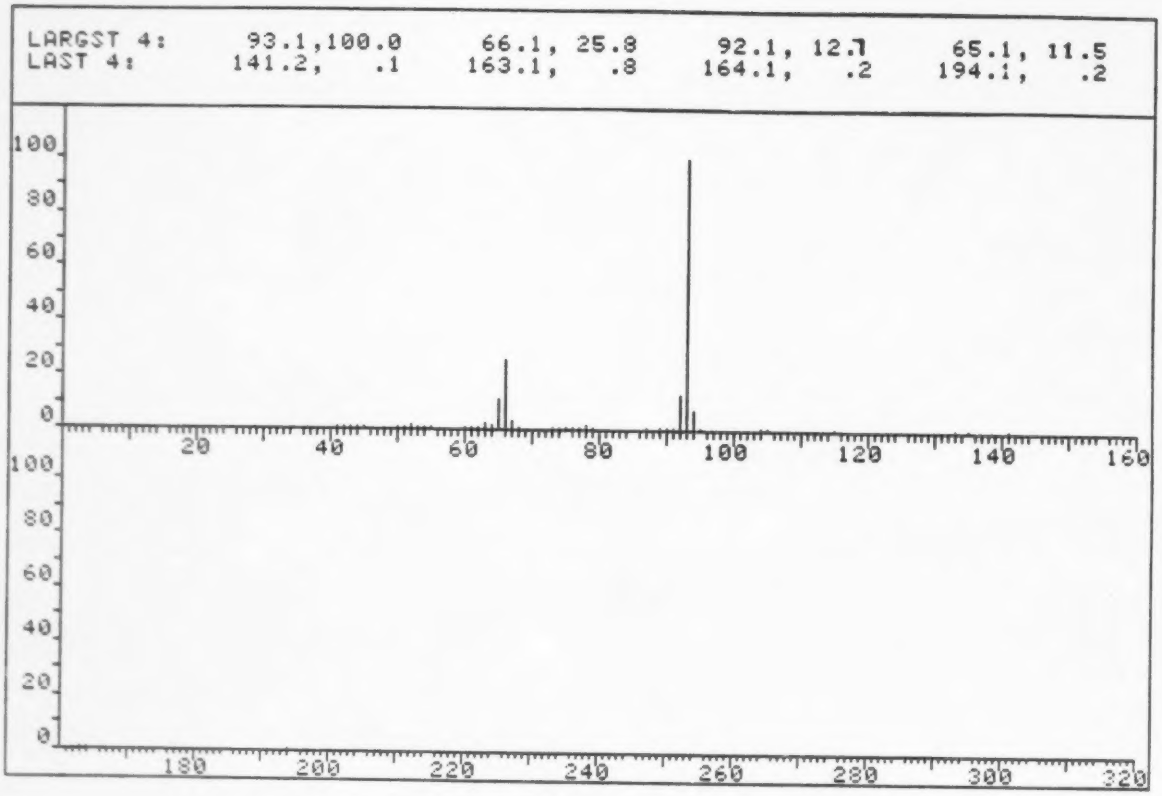


Figure B-10. Chromatogram by GC/MS for

(A) aniline(t_R = 4.3 min),
(B) O,O,O-triethyl phosphorothioate(t_R = 7.2 min), and
(C) p-dimethylaminoazobenzene(t_R = 19.8 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:      93.1,100.0       66.1, 25.8       92.1, 12.7        65.1, 11.5
LAST 4:       141.2,    .1     163.1,    .8     164.1,    .2      194.1,    .2
```

Figure B-11. Mass spectrum for aniline.

TABLE B-5. KEY IONS AND RELATIVE ABUNDANCES FOR ANILINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.1	.5	64.1	1.7	91.1	1.0
42.2	.2	65.1	11.5	92.1	12.7
43.3	.1	66.1	25.8	93.1	100.0
44.1	.0	67.1	3.1	94.1	6.9
45.6	.2	68.1	.2	95.1	.4
50.1	.8	73.0	.3	104.1	.2
51.1	.6	74.0	1.0	105.1	.2
52.1	1.5	75.1	.5	115.1	.1
53.1	.5	76.1	1.0	133.0	.1
54.1	1.2	77.1	.9	135.0	.1
55.1	.1	78.1	1.4	141.2	.1
60.0	.2	79.1	.2	163.1	.8
61.1	.8	87.1	.1	164.1	.2
62.1	1.3	89.1	.2	194.1	.2
63.1	2.6	90.1	.3		

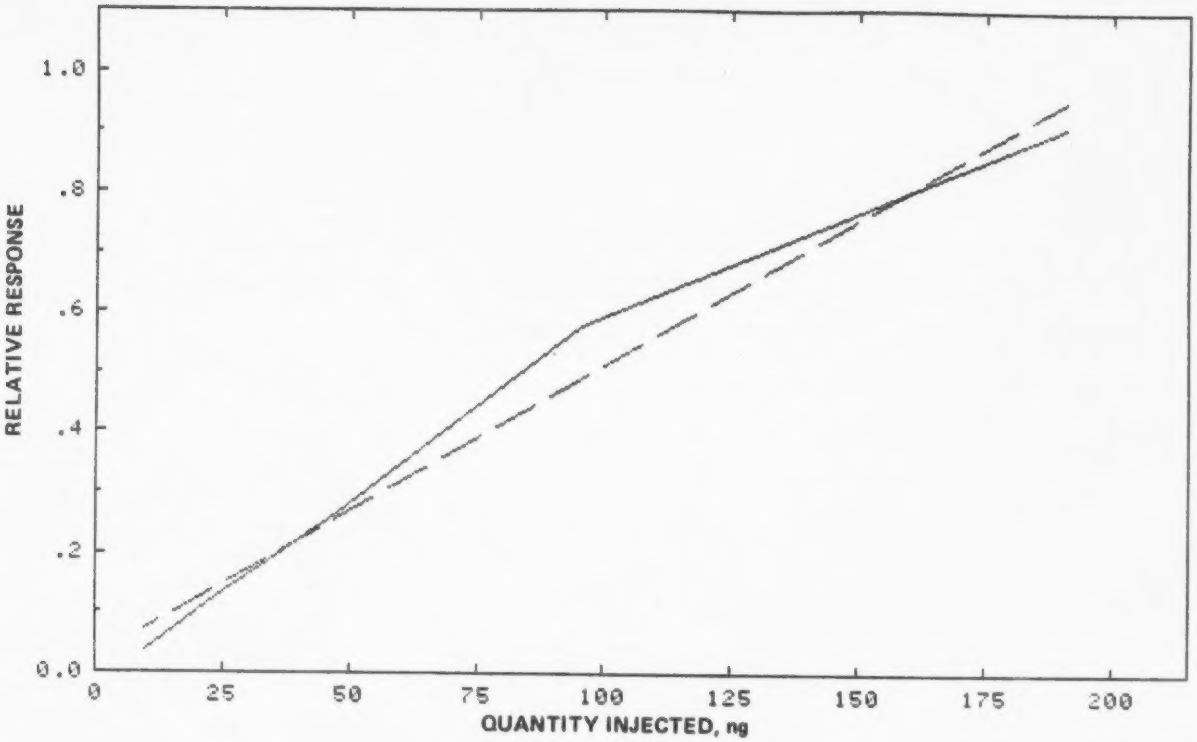
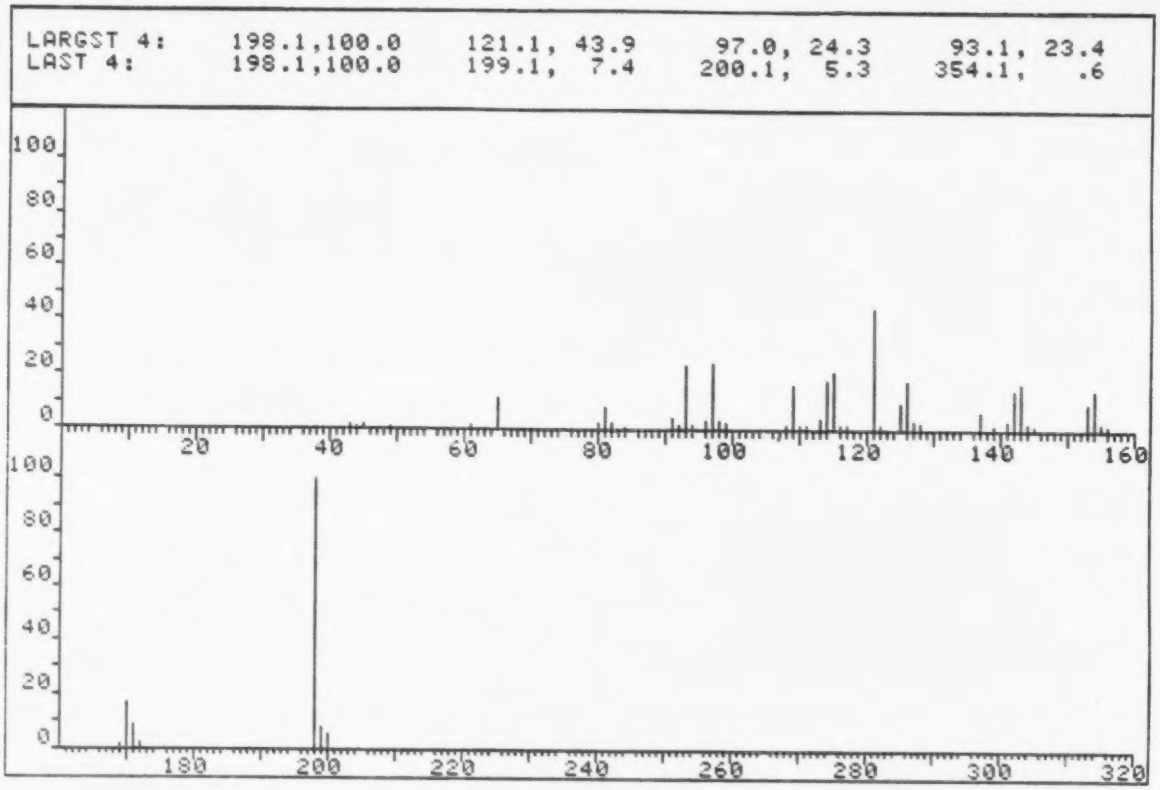


Figure B-12. Calibration curve for the determination of aniline by GC/MS.

Range: 24 - 190 ng
Correlation coefficient: 0.989
Slope: 4.8×10^{-3}
y-Intercept: 2.6×10^{-2}



```
LARGST 4:     198.1,100.0     121.1, 43.9      97.0, 24.3      93.1, 23.4
LAST 4:       198.1,100.0     199.1,  7.4     200.1,  5.3     354.1,    .6
```

Figure B-13. Mass spectrum for O,O,O-triethyl phosphorothioate.

TABLE B-6. KEY IONS AND RELATIVE ABUNDANCES FOR O,O,O-TRIETHYL PHOSPHOROTHIOATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
42.9	1.5	108.1	1.5	141.0	3.9
44.1	.3	109.1	16.3	142.0	14.5
45.2	1.8	110.1	1.5	143.0	16.9
49.0	.3	111.1	1.5	144.0	2.1
61.0	1.8	113.0	4.2	145.0	1.5
65.0	11.6	114.0	17.8	153.1	9.8
80.0	2.1	115.0	21.1	154.1	14.5
81.0	8.0	116.0	1.8	155.1	2.4
82.0	2.7	117.0	1.8	156.1	1.5
84.0	.3	121.1	43.9	169.1	1.5
91.1	4.2	122.1	1.8	170.1	16.6
91.9	1.8	125.0	9.5	171.1	8.9
93.1	23.4	126.0	18.1	172.1	1.8
94.1	1.8	127.0	3.3	198.1	100.0
95.9	3.6	128.0	2.7	199.1	7.4
97.0	24.3	137.0	6.2	200.1	5.3
98.0	3.6	139.0	1.5	354.1	.6
98.9	2.1				

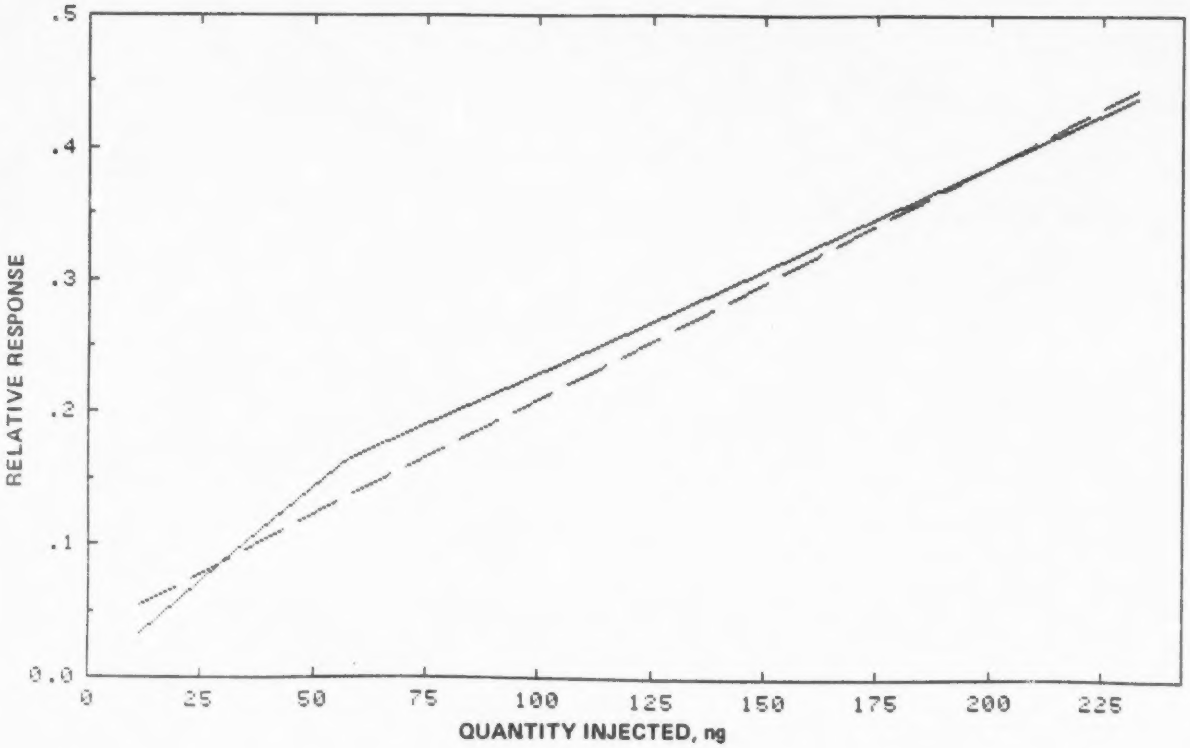
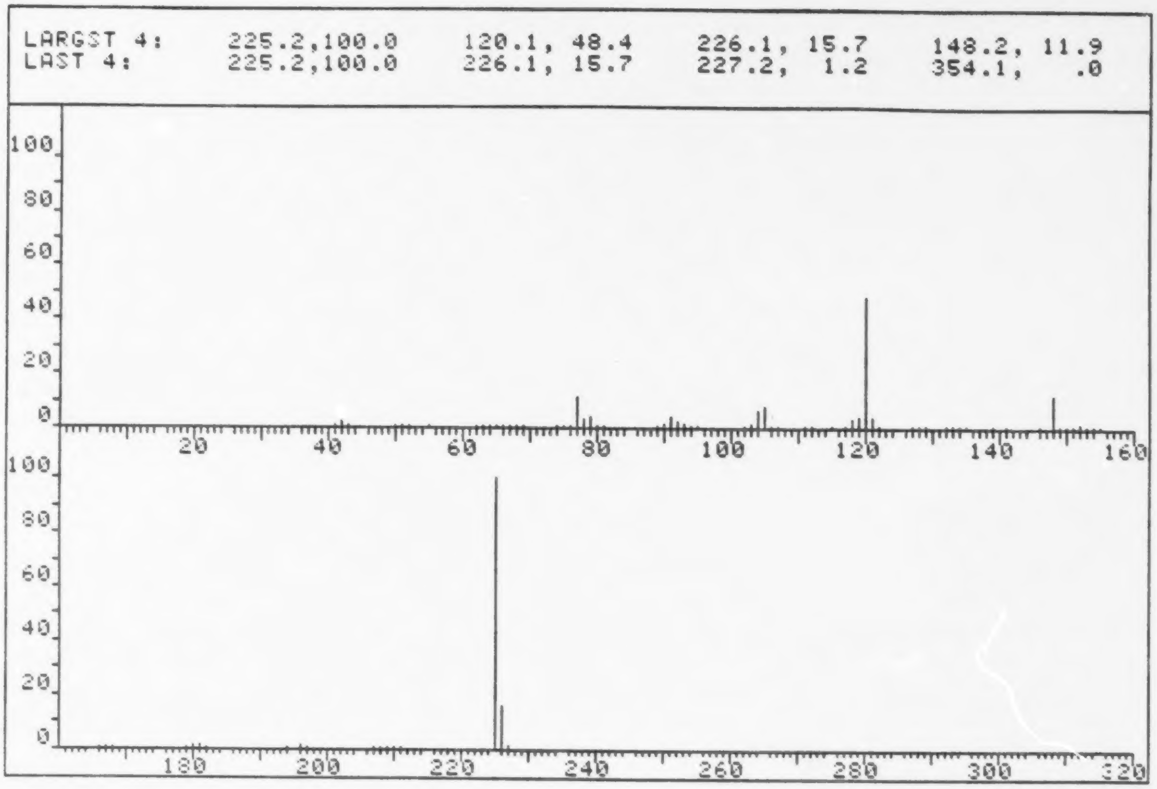


Figure B-14. Calibration curve for the determination of O,O,O-triethyl phosphorothioate by GC/MS.

Range: 29 - 230 ng
Correlation coefficient: 0.993
Slope: 1.8 x 10^{-3}
y-Intercept: 3.4 x 10^{-2}



```
LARGST 4:    225.2,100.0    120.1, 48.4    226.1, 15.7    148.2, 11.9
LAST 4:      225.2,100.0    226.1, 15.7    227.2,  1.2    354.1,   .0
```

Figure B-15. Mass spectrum for p-dimethylaminoazobenzene.

TABLE B-7. KEY IONS AND RELATIVE ABUNDANCES FOR *p*-DIMETHYLAMINOAZOBENZENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.2	.1	94.1	.7	148.2	11.9
42.1	2.5	95.1	.2	149.2	1.2
43.1	.2	102.1	.3	150.1	.2
50.1	.2	103.1	1.4	151.1	.4
51.1	.5	104.1	6.6	152.1	1.8
52.1	.4	105.1	8.6	153.1	1.0
55.0	.2	106.1	.9	154.1	.4
62.1	.2	107.1	.2	155.2	.2
63.0	.9	111.6	.2	166.1	.2
64.0	.7	112.6	1.2	167.1	.3
65.1	1.0	115.1	.4	168.1	.2
66.0	.5	117.1	.7	179.1	.2
67.1	.3	118.1	3.4	180.1	.9
68.1	.3	119.1	4.1	181.1	1.0
69.1	.1	120.1	48.4	182.1	.3
74.0	.3	121.1	4.3	194.2	.2
75.0	.4	122.1	.3	196.2	.9
76.0	1.0	127.2	.3	197.2	.3
77.1	11.0	128.2	.3	207.0	.2
78.1	3.1	129.1	.2	208.1	.2
79.1	4.2	132.2	.4	209.1	.4
80.1	.9	133.2	.7	210.2	.3
81.1	.3	134.2	.4	211.1	.2
89.1	.3	135.2	.2	225.2	100.0
90.1	1.6	139.0	.2	226.1	15.7
91.1	4.0	141.2	.2	227.2	1.2
92.1	2.4	146.0	.3	354.1	.0
93.1	1.8				

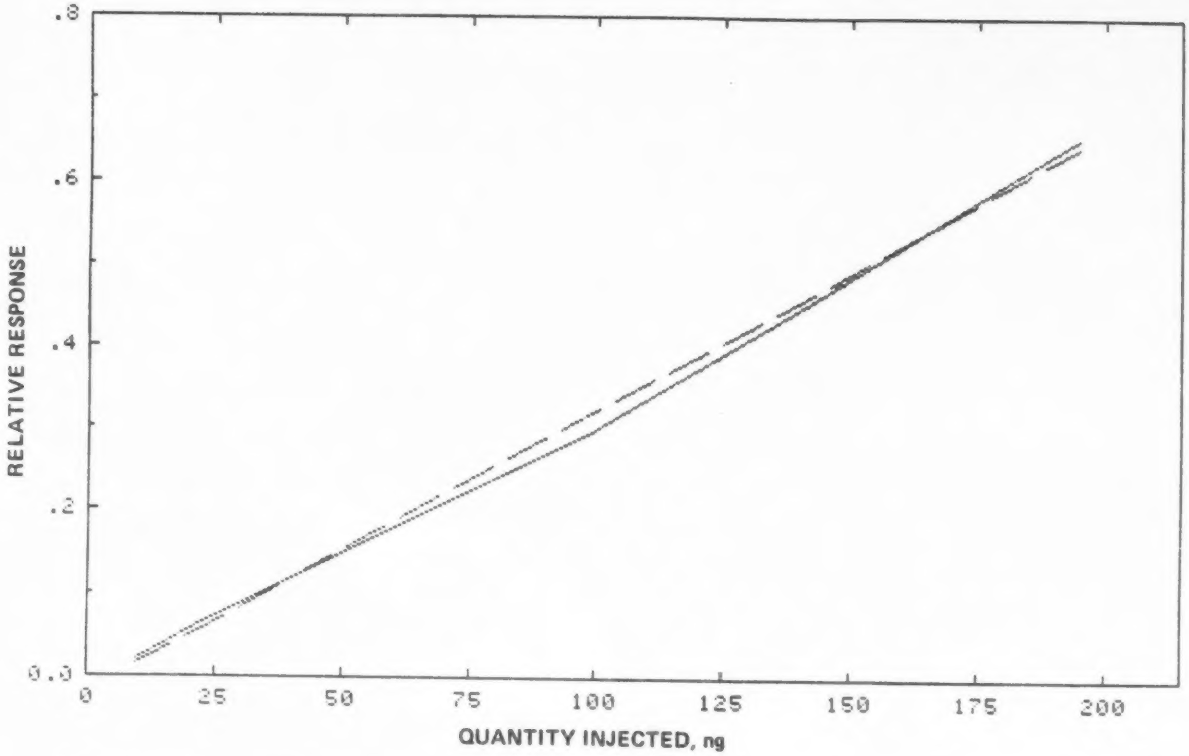


Figure B-16. Calibration curve for the determination of p-dimethylaminoazobenzene by GC/MS.

Range: 24 - 200 ng
Correlation coefficient: 0.999
Slope: 3.4×10^{-3}
y-Intercept: -1.8×10^{-2}

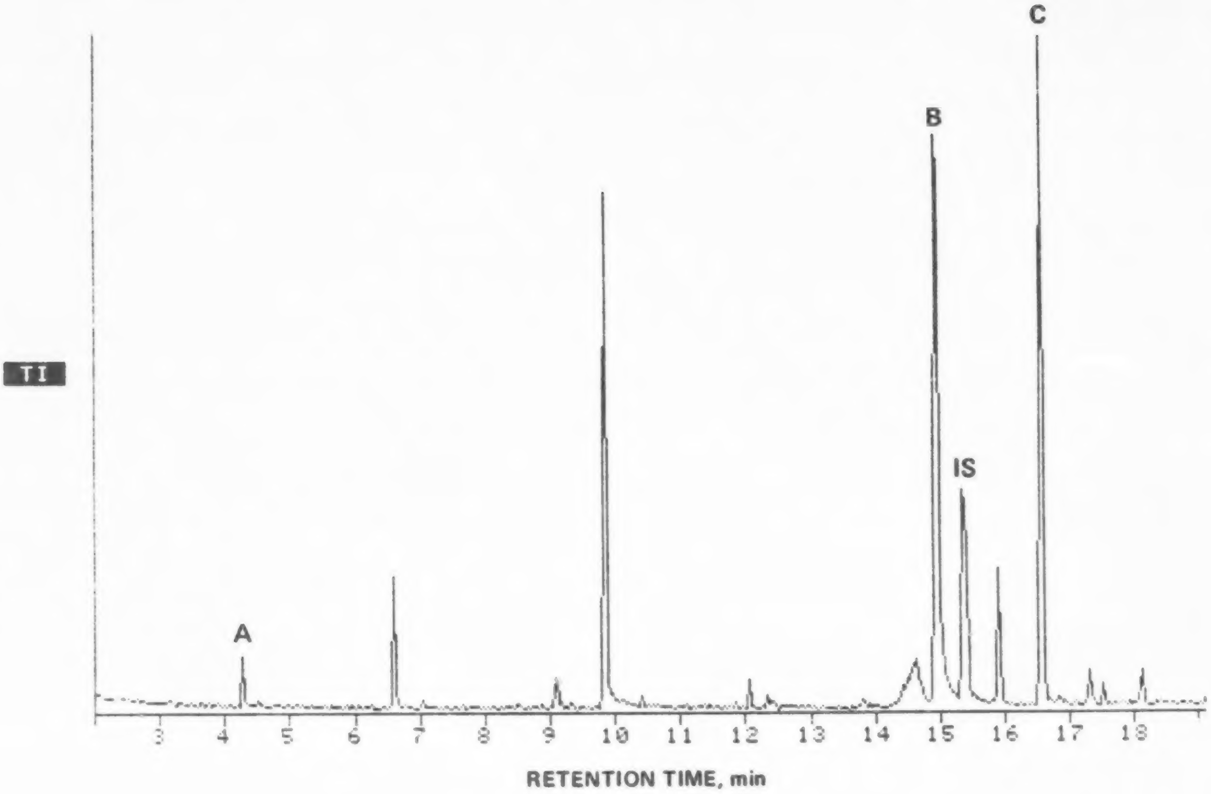
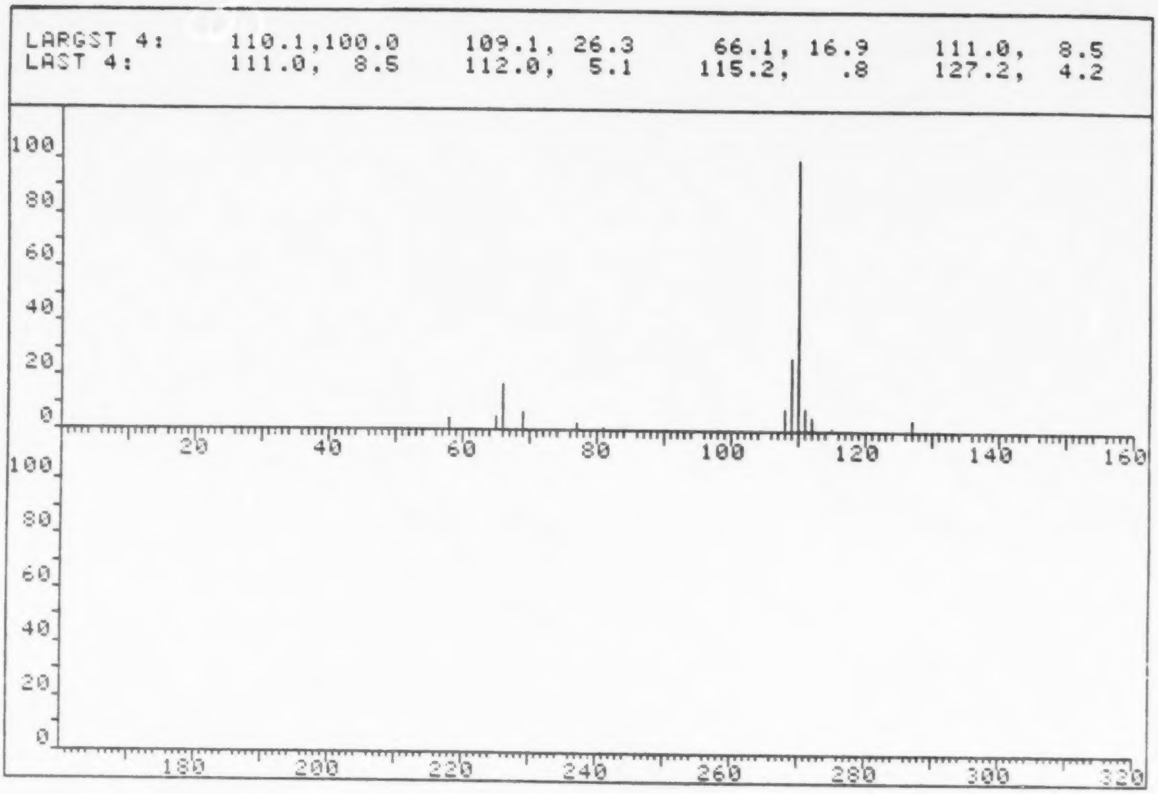


Figure B-17. Chromatogram by GC/MS for

(A) benzenethiol(t_R = 4.1 min),
(B) octamethyl pyrophosphoramide(t_R = 14.8 min), and
(C) methyl parathion(t_R = 16.4 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:    110.1,100.0      109.1, 26.3       66.1, 16.9      111.0,  8.5
LAST 4:      111.0,  8.5      112.0,  5.1      115.2,    .8     127.2,  4.2
```

Figure B-18. Mass spectrum for benzenethiol.

TABLE B-8. KEY IONS AND RELATIVE ABUNDANCES FOR BENZENETHIOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
57.9	4.2	81.0	.8	111.0	8.5
65.1	5.1	108.1	7.6	112.0	5.1
66.1	16.9	109.1	26.3	115.2	.8
69.1	6.8	110.1	100.0	127.2	4.2
77.1	2.5				

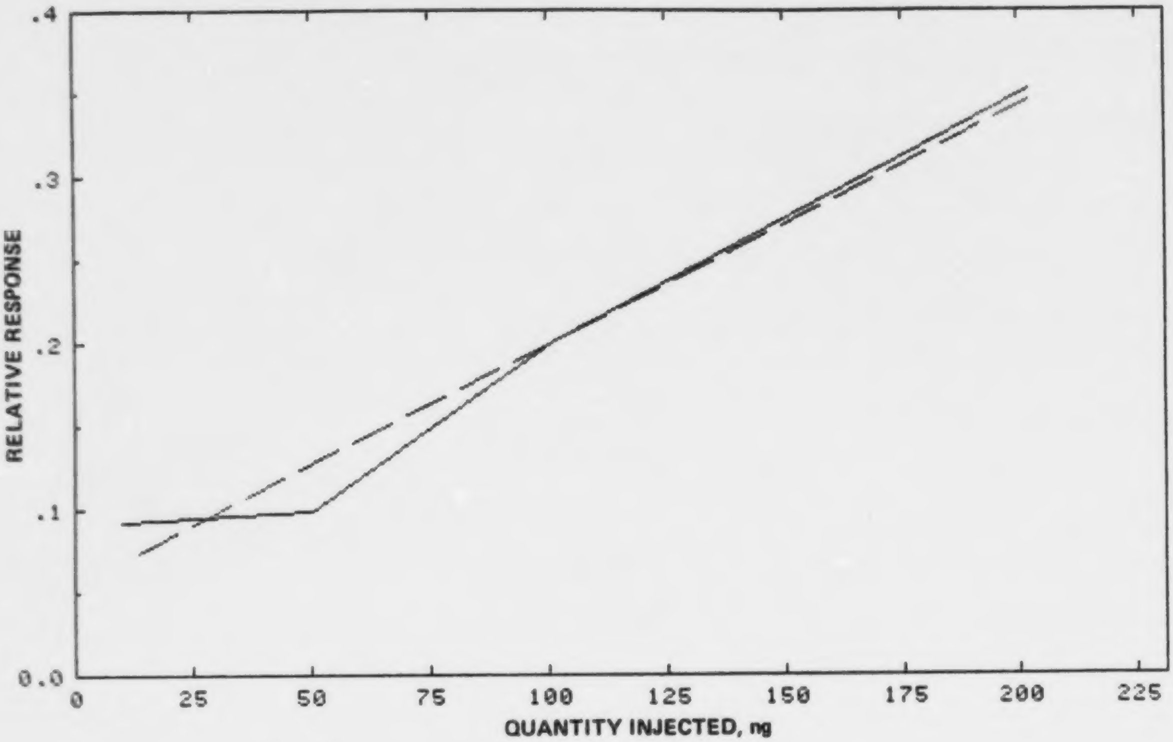
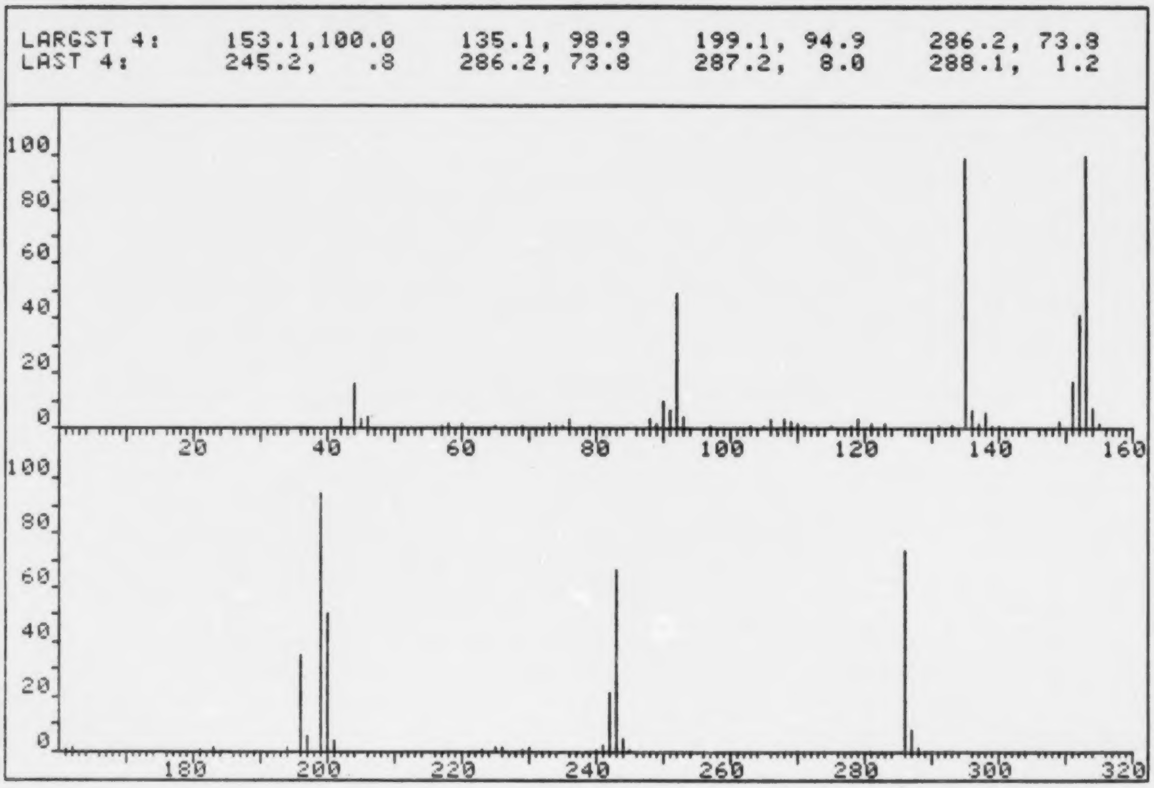


Figure B-19. Calibration curve for the determination of benzenethiol by GC/MS.

Range: 50 - 200 ng
Correlation coefficient: 0.984
Slope: 1.4×10^{-3}
y-Intercept: 5.4×10^{-2}



```
LARGST 4:    153.1,100.0    135.1, 98.9    199.1, 94.9    286.2, 73.8
LAST 4:      245.2,    .8   286.2, 73.8    287.2,  8.0    288.1,  1.2
```

Figure B-20. Mass spectrum for octamethyl pyrophosphoramide .

TABLE B-9. KEY IONS AND RELATIVE ABUNDANCES FOR OCTAMETHYL PYROPHOSPHORAMIDE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
42.1	3.0	108.1	3.6	162.2	1.1
44.2	16.3	109.1	2.5	181.2	.7
45.2	2.9	110.0	1.4	182.9	1.0
46.2	4.4	111.0	.8	194.2	1.0
57.2	1.0	115.1	.3	196.2	35.1
58.1	1.7	118.3	.7	197.2	5.1
60.0	1.9	119.1	2.9	199.1	94.9
65.1	1.0	121.2	1.7	200.1	50.3
69.1	.8	123.1	1.7	201.1	3.6
73.1	1.7	131.2	.8	223.3	.7
74.2	.7	133.2	1.0	225.1	1.1
75.1	1.1	135.1	98.9	226.1	1.7
76.1	3.0	136.1	6.2	229.0	.7
79.0	.7	137.1	1.5	230.2	1.1
88.2	3.3	138.1	5.5	240.2	.8
89.2	1.4	139.2	.6	241.2	2.2
90.1	9.5	140.1	.8	242.2	21.1
91.2	6.6	149.1	2.3	243.2	66.6
92.1	49.3	151.1	17.4	244.2	4.6
93.1	4.6	152.2	40.7	245.2	.8
97.1	.7	153.1	100.0	286.2	73.8
103.0	.7	154.1	6.9	287.2	8.0
105.2	.7	155.1	1.7	288.1	1.2
106.2	3.9	161.1	.7		

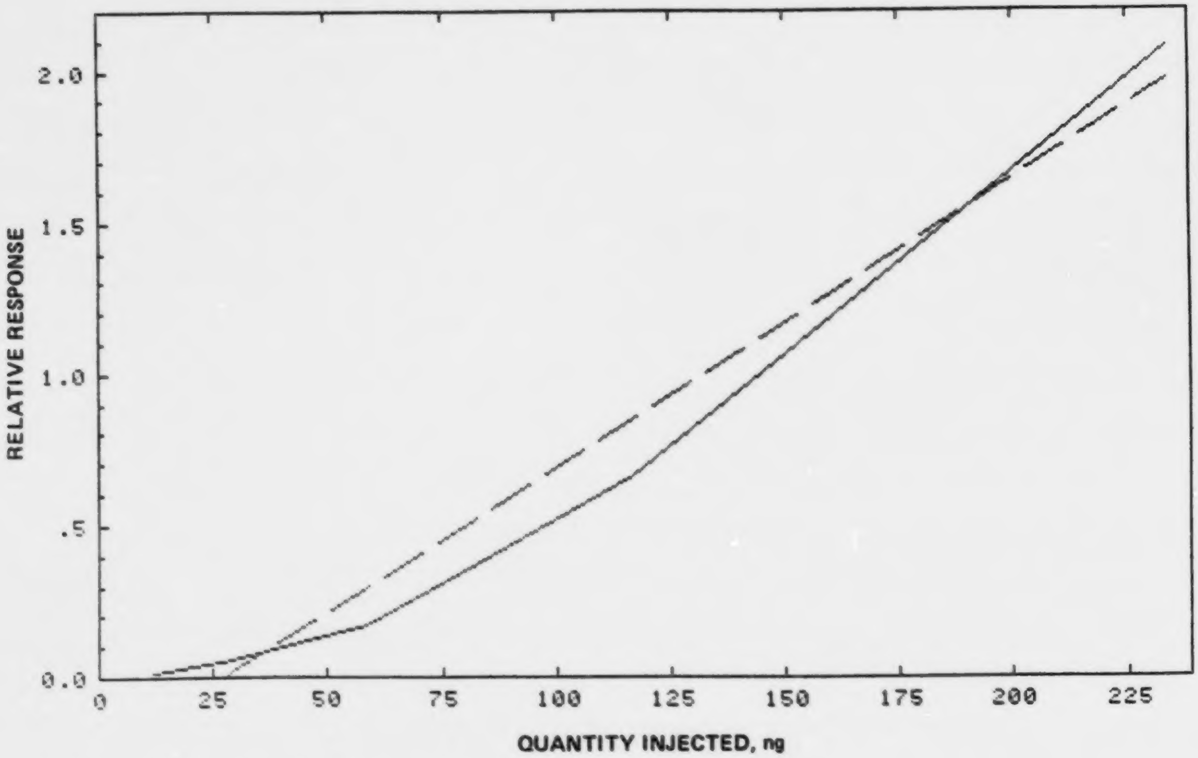
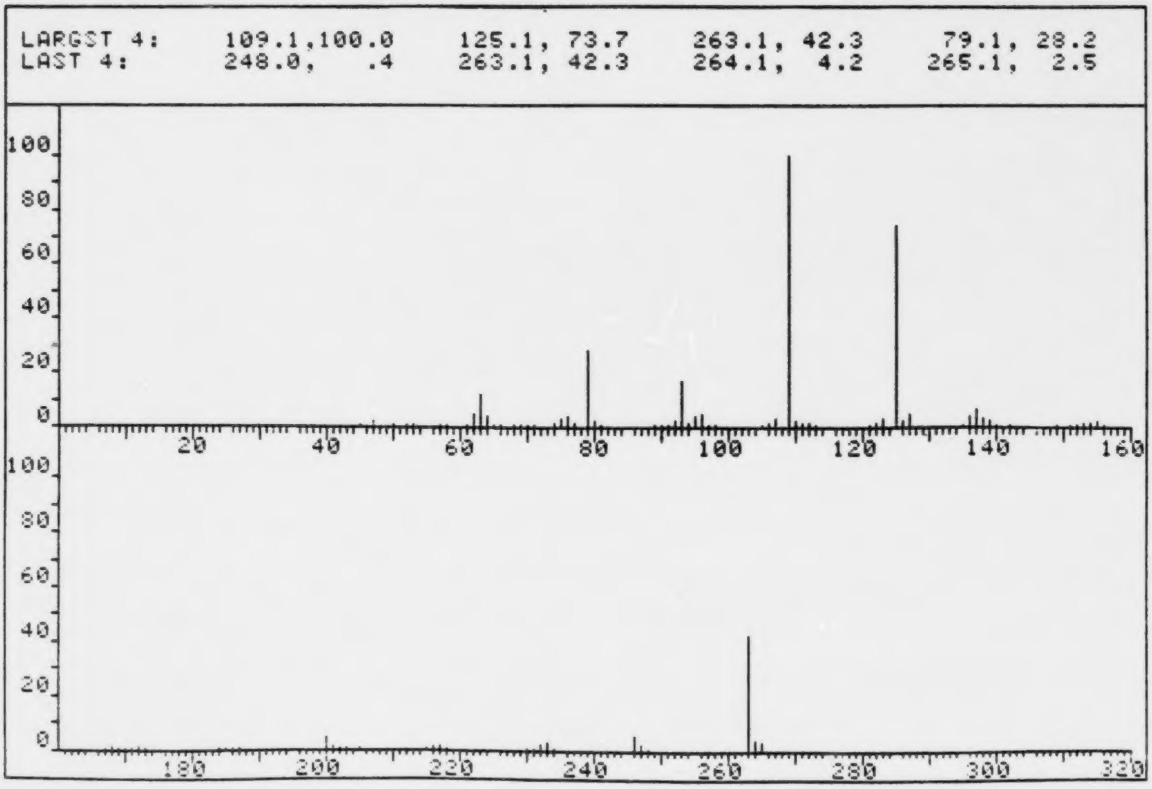


Figure B-21. Calibration curve for the determination of octamethyl pyrophosphoramide by GC/MS.

Range: 120 - 230 ng
Correlation coefficient: 0.985
Slope: 9.5×10^{-3}
y-Intercept: -2.6×10^{-1}



```
LARGST 4:    109.1,100.0    125.1, 73.7    263.1, 42.3     79.1, 28.2
LAST 4:      248.0,    .4   263.1, 42.3    264.1,  4.2    265.1,  2.5
```

Figure B-22. Mass spectrum for methyl parathion.

TABLE B-10. KEY IONS AND RELATIVE ABUNDANCES FOR METHYL PARATHION

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
45.1	.4	96.1	4.8	167.1	.6
47.1	2.6	97.1	.6	168.2	1.0
50.1	1.1	98.1	.3	169.2	.4
52.1	.4	105.0	.3	170.0	.6
53.1	.3	106.1	1.6	171.0	.6
57.0	.3	107.1	2.9	172.0	1.2
58.1	.3	109.1	100.0	173.0	.3
61.0	.4	110.2	2.5	184.2	.3
62.1	4.9	111.1	2.0	185.1	.8
63.1	12.1	112.0	1.5	186.0	.6
64.1	4.5	113.0	.4	187.1	.4
65.1	1.1	121.2	.6	200.1	4.7
66.1	.3	122.1	1.7	201.1	1.0
68.1	.6	123.1	3.2	202.1	.6
69.1	1.1	125.1	73.7	202.9	.3
70.1	.2	126.1	2.2	205.1	.7
71.3	.3	127.1	4.9	215.1	.4
74.1	1.6	135.1	.8	216.1	1.5
75.1	3.4	136.1	4.5	217.1	1.1
76.1	3.9	137.1	6.8	218.1	.7
77.1	1.7	138.1	2.9	230.2	.3
79.1	28.2	139.1	2.5	231.2	.5
80.0	2.1	140.2	.6	232.0	2.3
81.1	.3	142.1	.4	233.1	2.9
89.2	.8	149.1	.3	234.1	.3
90.1	.7	151.2	.7	246.1	5.3
91.2	1.1	152.1	1.0	247.1	2.1
92.1	2.6	153.1	2.0	248.0	.4
93.1	17.0	154.1	1.7	263.1	42.3
94.0	1.6	155.1	2.7	264.1	4.2
95.0	4.0	156.1	.1	265.1	2.5

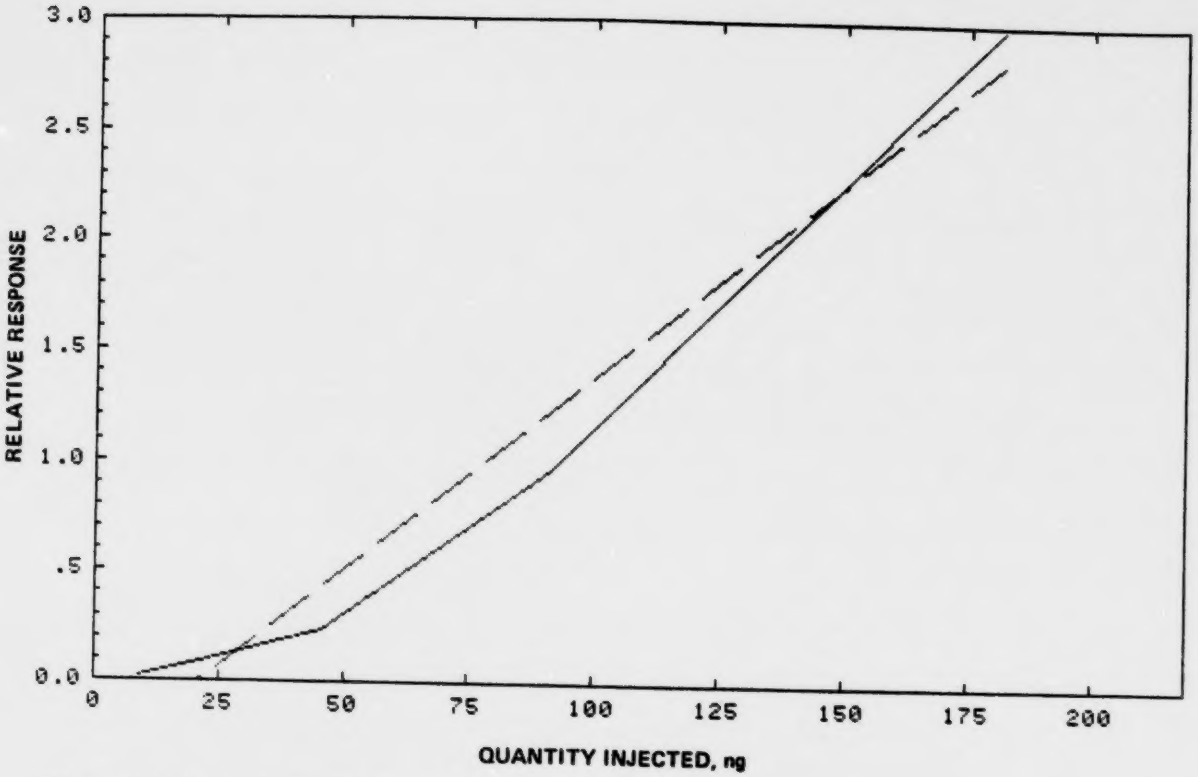


Figure B-23. Calibration curve for the determination of methyl parathion by GC/MS.

Range: 91 - 180 ng
Correlation coefficient: 0.984
Slope: 1.8 x 10^{-2}
y-Intercept: -3.7 x 10^{-1}

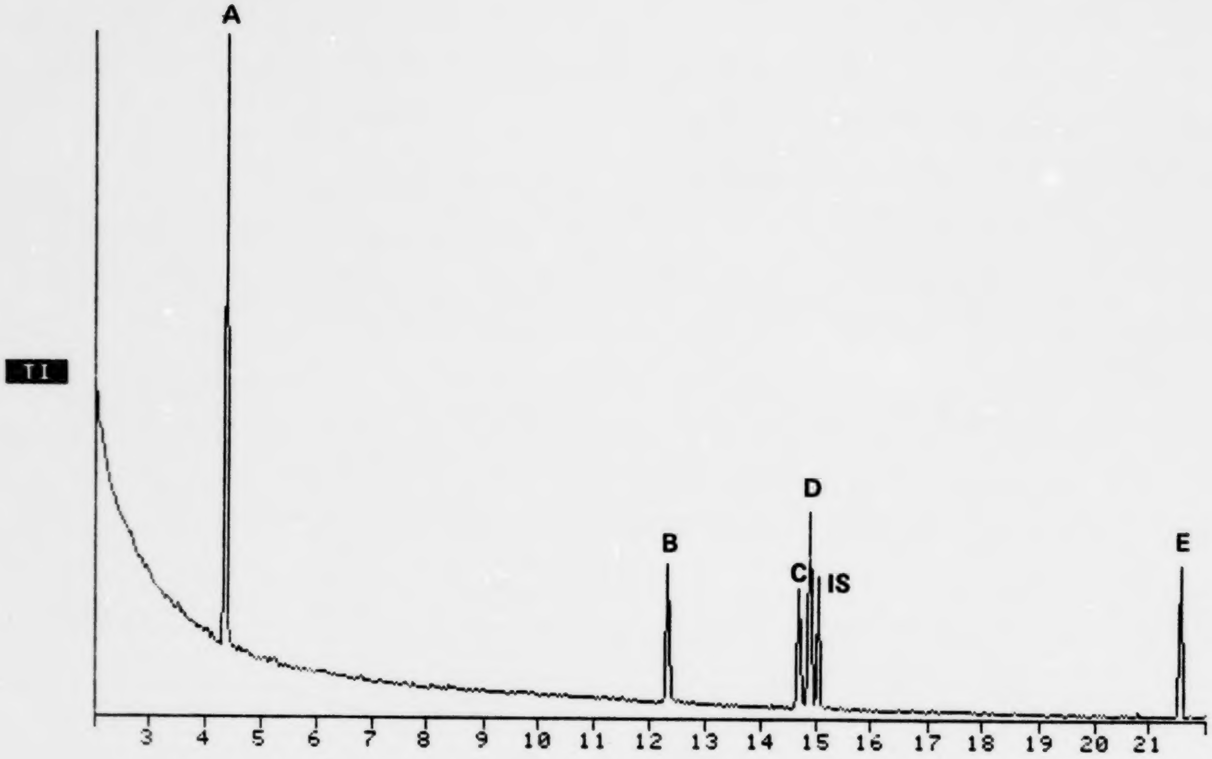
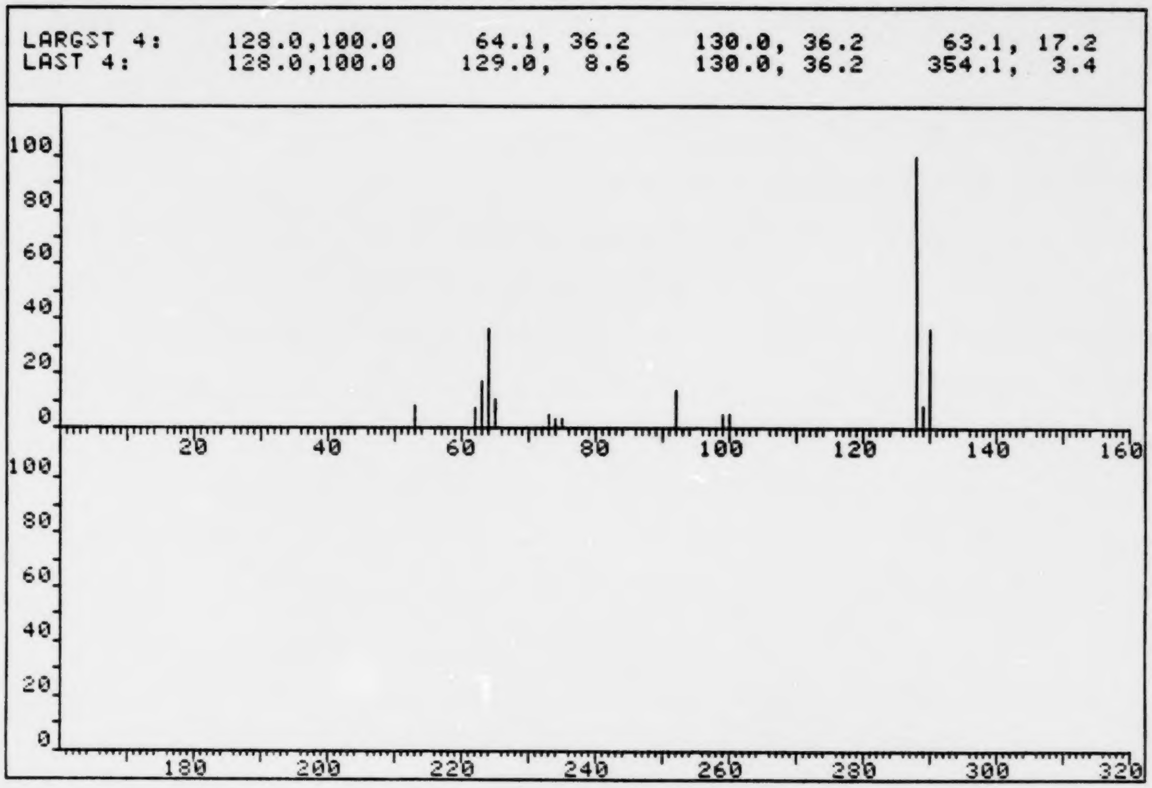


Figure B-24. Chromatogram by GC/MS for

(A) 2-chlorophenol(t_R = 4.5 min),
(B) 2,3,4,6-tetrachlorophenol(t_R = 12.5 min),
(C) pentachlorophenol(t_R = 15.0 min),
(D) pentachloronitrobenzene(t_R = 15.2 min), and
(E) methoxychlor(t_R = 21.8 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:     128.0,100.0      64.1, 36.2     130.0, 36.2      63.1, 17.2
LAST 4:       128.0,100.0     129.0,  8.6     130.0, 36.2     354.1,  3.4
```

Figure B-25. Mass spectrum for 2-chlorophenol.

TABLE B-11. KEY IONS AND RELATIVE ABUNDANCES FOR 2-CHLOROPHENOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
53.2	8.6	73.0	5.2	100.0	5.2
62.1	6.9	74.1	3.4	128.0	100.0
63.1	17.2	74.9	3.4	129.0	8.6
64.1	36.2	91.9	13.8	130.0	36.2
65.1	10.3	99.0	5.2	354.1	3.4

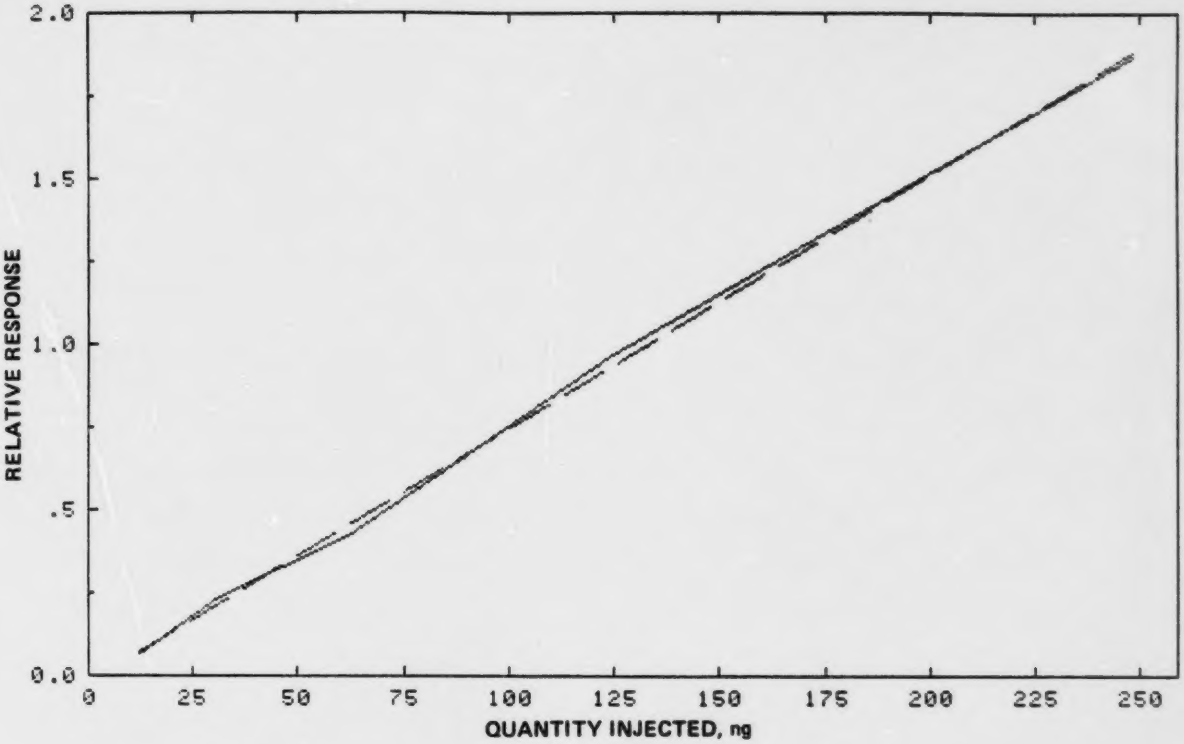
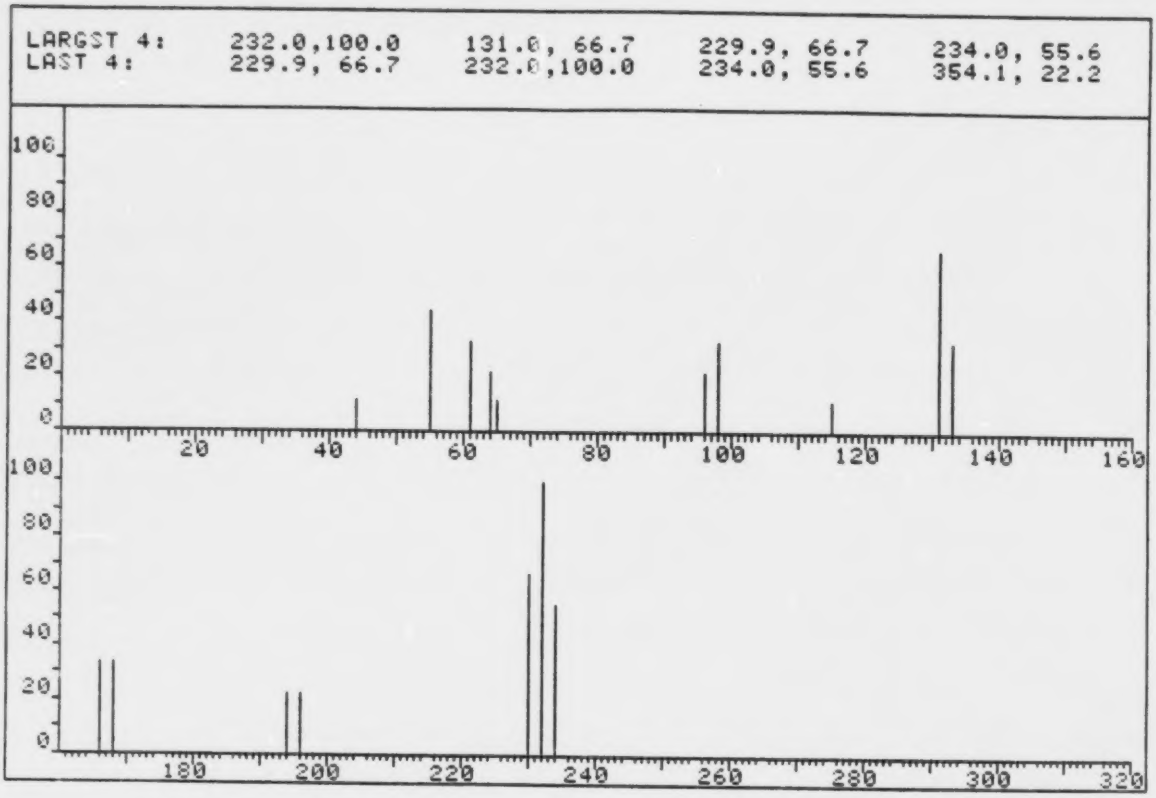


Figure B-26. Calibration curve for the determination of 2-chlorophenol by GC/MS.

Range: 12 - 250 ng
Correlation coefficient: 0.999
Slope: 7.6×10^{-3}
y-Intercept: -1.9×10^{-2}



```
LARGST 4:     232.0,100.0     131.0, 66.7     229.9, 66.7     234.0, 55.6
LAST 4:       229.9, 66.7     232.0,100.0     234.0, 55.6     354.1, 22.2
```

Figure B-27. Mass spectrum for 2,3,4,6-tetrachlorophenol.

TABLE B-12. KEY IONS AND RELATIVE ABUNDANCES FOR 2,3,4,6-TETRACHLOROPHENOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
44.0	11.1	98.1	33.3	194.0	22.2
55.0	44.4	115.0	11.1	196.0	22.2
61.1	33.3	131.0	66.7	229.9	66.7
63.9	22.2	133.0	33.3	232.0	100.0
65.0	11.1	165.9	33.3	234.0	55.6
96.2	22.2	167.9	33.3	354.1	22.2

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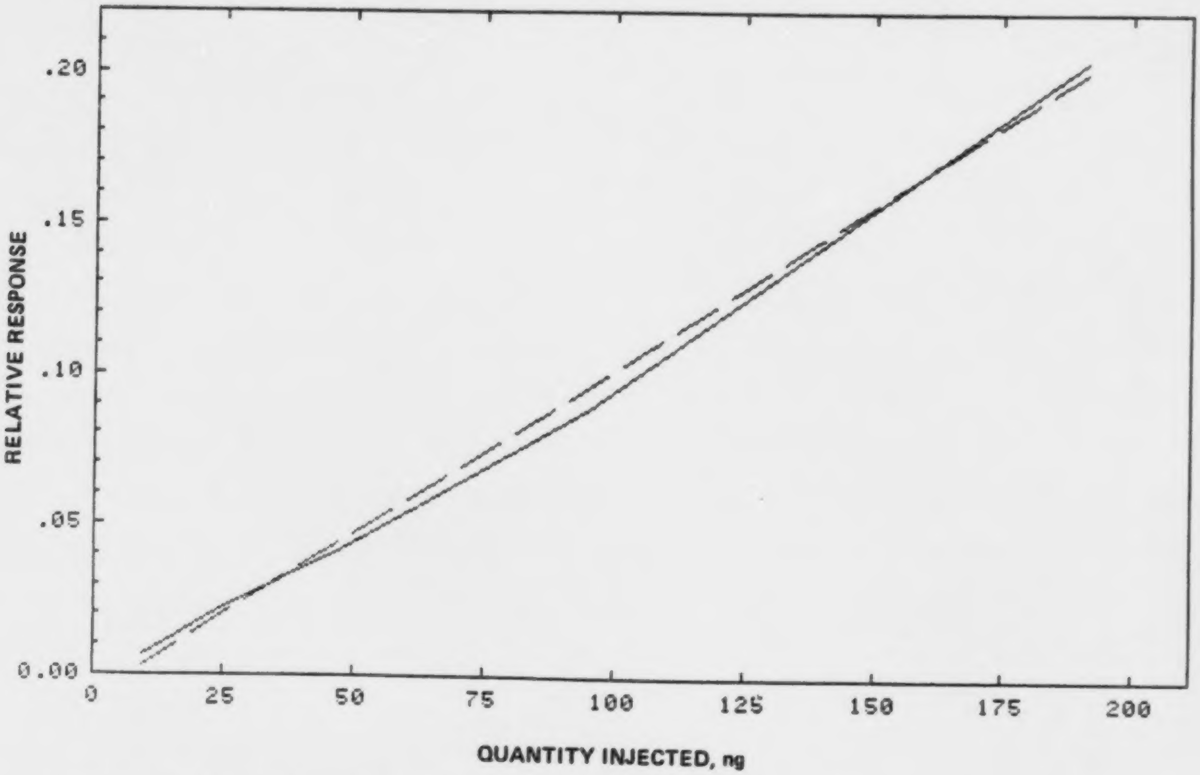
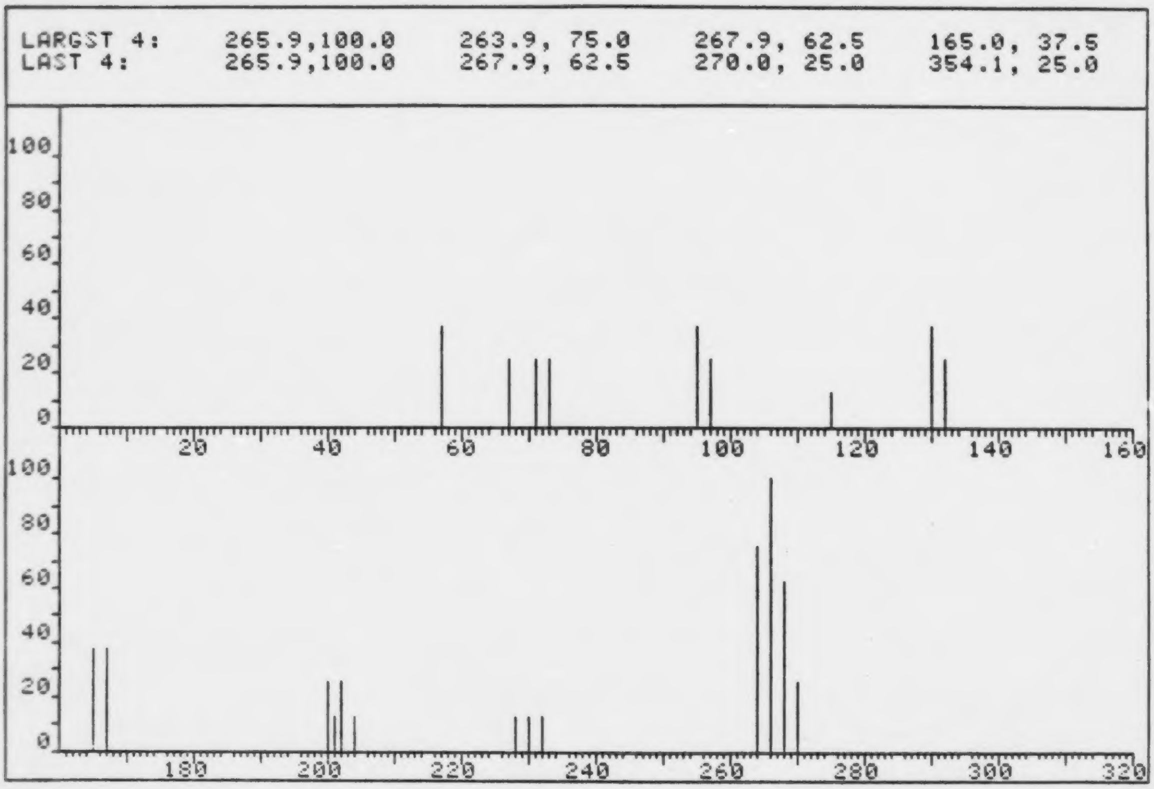


Figure B-28. Calibration curve for the determination of 2,3,4,6-tetrachlorophenol by GC/MS.

Range: 24 - 190 ng
Correlation coefficient: 0.998
Slope: 1.1×10^{-3}
y-Intercept: -7.1×10^{-3}



```
LARGST 4:    265.9,100.0    263.9, 75.0    267.9, 62.5    165.0, 37.5
LAST 4:      265.9,100.0    267.9, 62.5    270.0, 25.0    354.1, 25.0
```

Figure B-29. Mass spectrum for pentachlorophenol.

TABLE B-13. KEY IONS AND RELATIVE ABUNDANCES FOR PENTACHLOROPHENOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
57.0	37.5	131.8	25.0	230.0	12.5
66.8	25.0	165.0	37.5	231.9	12.5
71.1	25.0	166.9	37.5	263.9	75.0
73.0	25.0	200.0	25.0	265.9	100.0
95.0	37.5	200.8	12.5	267.9	62.5
97.1	25.0	201.9	25.0	270.0	25.0
115.1	12.5	203.9	12.5	354.1	25.0
129.9	37.5	228.0	12.5		

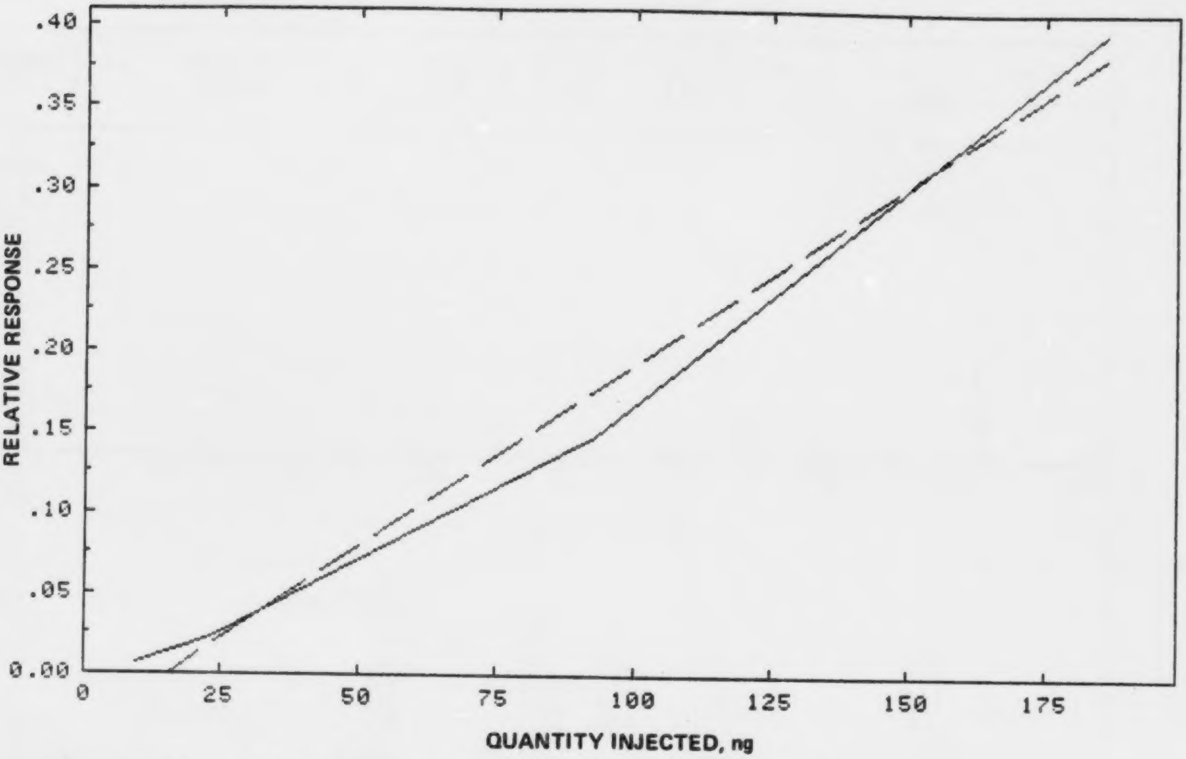
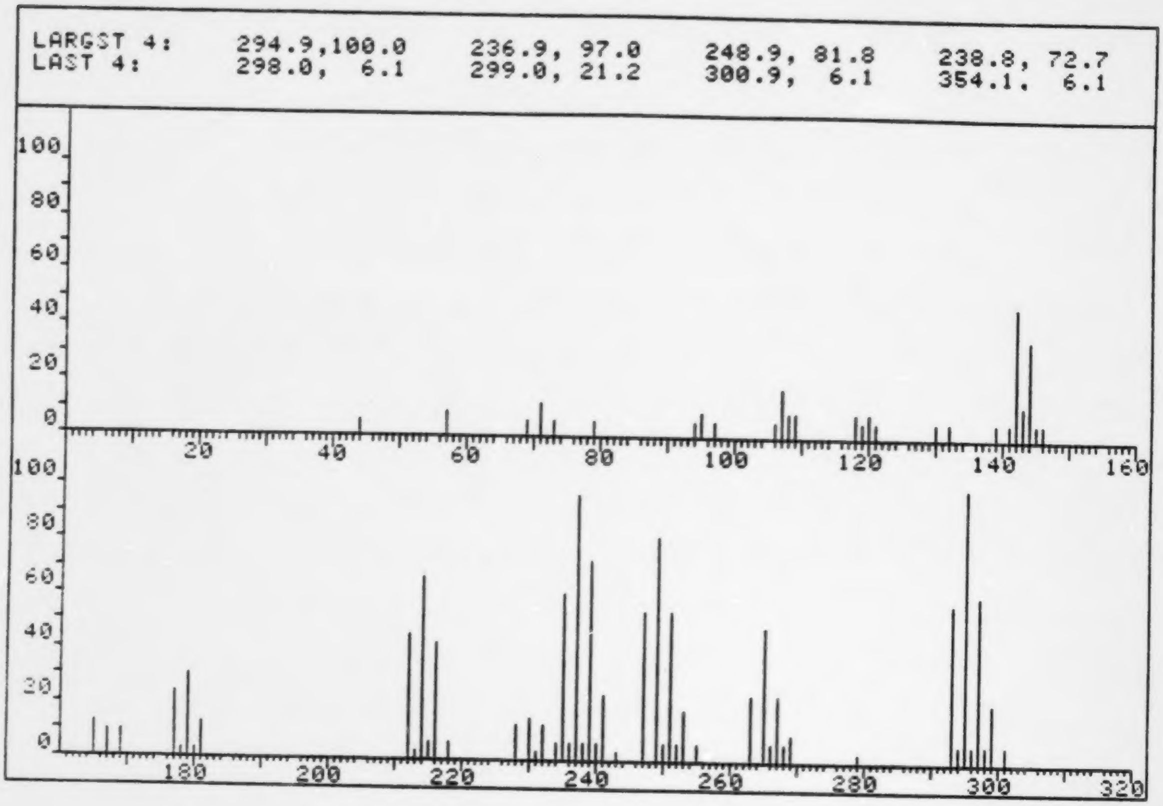


Figure B-30. Calibration curve for the determination of pentachlorophenol by GC/MS.

Range: 23 - 190 ng
Correlation coefficient: 0.993
Slope: 2.2 x 10^{-3}
y-Intercept: -3.2 x 10^{-2}



```
LARGST 4:     294.9,100.0      236.9, 97.0      248.9, 81.8      238.8, 72.7
LAST 4:       298.0,   6.1     299.0, 21.2      300.9,   6.1     354.1,   6.1
```

Figure B-31. Mass spectrum for pentachloronitrobenzene.

TABLE B-14. KEY IONS AND RELATIVE ABUNDANCES FOR PENTACHLORONITROBENZENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.9	6.1	164.9	12.1	240.8	24.2
57.1	9.1	166.9	9.1	242.8	3.0
69.2	6.1	169.0	9.1	246.8	54.5
70.9	12.1	176.9	24.2	248.9	81.8
73.0	6.1	178.0	3.0	249.9	6.1
78.9	6.1	179.0	30.3	250.8	54.5
93.9	6.1	180.0	3.0	251.8	6.1
94.9	9.1	181.0	12.1	252.9	18.2
97.1	6.1	211.9	45.5	254.8	6.1
105.9	6.1	212.9	3.0	262.9	24.2
107.1	18.2	213.9	66.7	264.9	48.5
108.1	9.1	214.9	6.1	265.9	6.1
109.1	9.1	215.9	42.4	266.9	24.2
118.0	9.1	217.9	6.1	267.9	6.1
119.0	6.1	227.9	12.1	268.9	9.1
120.0	9.1	230.0	15.2	279.0	3.0
121.1	6.1	231.2	3.0	292.9	57.6
129.8	6.1	231.9	12.1	293.8	6.1
132.0	6.1	234.0	6.1	294.9	100.0
139.0	6.1	234.9	60.6	295.9	6.1
141.0	6.1	235.9	6.1	296.9	60.6
141.9	48.5	236.9	97.0	298.0	6.1
143.0	12.1	237.9	6.1	299.0	21.2
144.0	36.4	238.8	72.7	300.9	6.1
145.0	6.1	239.8	6.1	354.1	6.1
146.0	6.1				

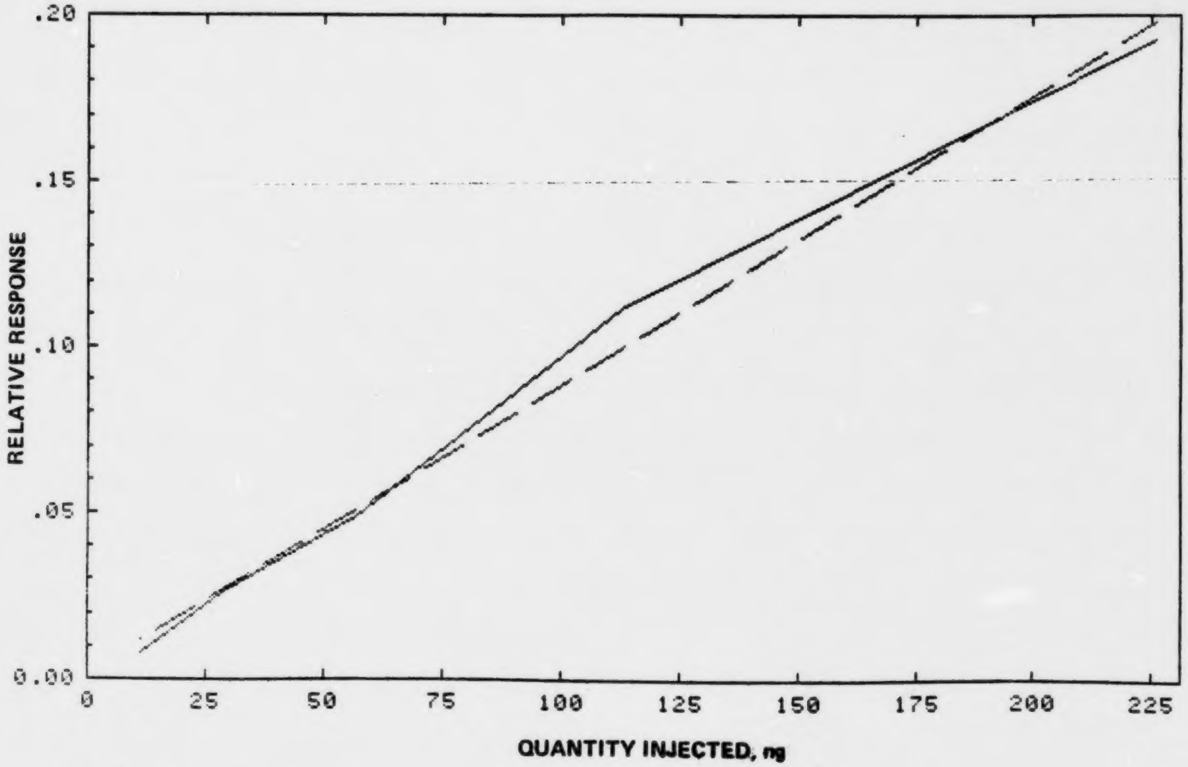
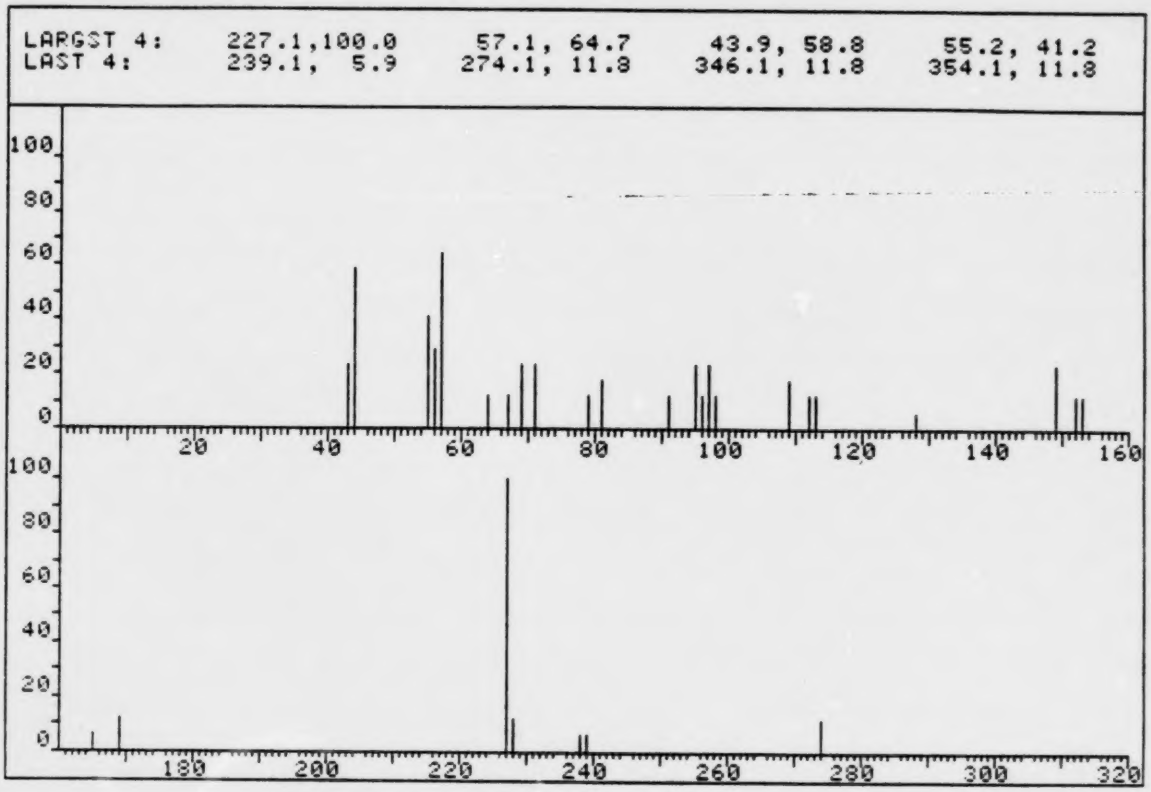


Figure B-32. Calibration curve for the determination of pentachloronitrobenzene by GC/MS.

Range: 29 - 230 ng
Correlation coefficient: 0.996
Slope: 8.7×10^{-4}
y-Intercept: 1.9×10^{-3}



```
LARGST 4:     227.1,100.0      57.1, 64.7      43.9, 58.8      55.2, 41.2
LAST 4:       239.1,   5.9    274.1, 11.8     346.1, 11.8     354.1, 11.8
```

Figure B-33. Mass spectrum for methoxychlor.

TABLE B-15. KEY IONS AND RELATIVE ABUNDANCES FOR METHOXYCHLOR

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.2	23.5	91.1	11.8	153.2	11.8
43.9	58.8	95.1	23.5	165.2	5.9
55.2	41.2	96.1	11.8	169.3	11.8
56.0	29.4	97.1	23.5	227.1	100.0
57.1	64.7	98.0	11.8	228.1	11.8
64.0	11.8	109.1	17.6	238.1	5.9
67.0	11.8	112.1	11.8	239.1	5.9
69.1	23.5	113.3	11.8	274.1	11.8
71.1	23.5	128.2	5.9	346.1	11.8
79.0	11.8	148.9	23.5	354.1	11.8
81.1	17.6	152.1	11.8		

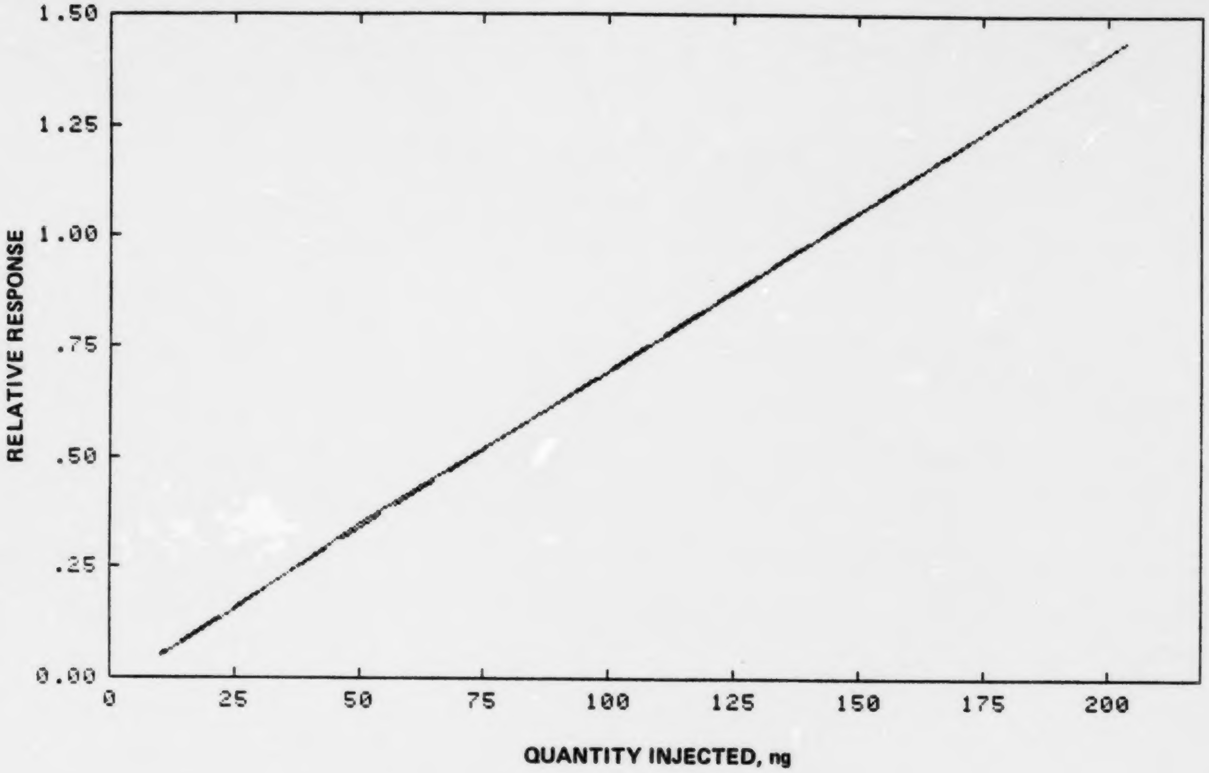


Figure B-34. Calibration curve for the determination of methoxychlor by GC/MS.

Range: 10 - 200 ng
Correlation coefficient: 0.999
Slope: 7.2 x 10^{-3}
y-Intercept: -2.1 x 10^{-2}

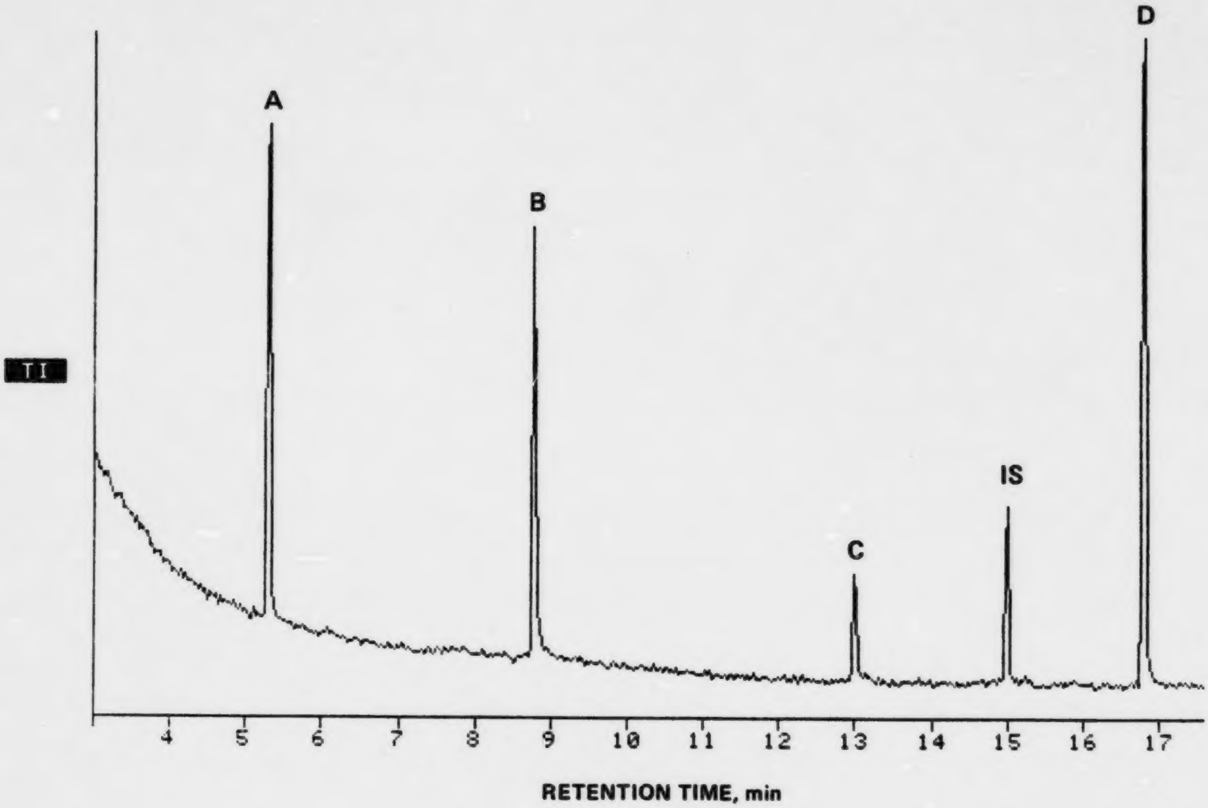
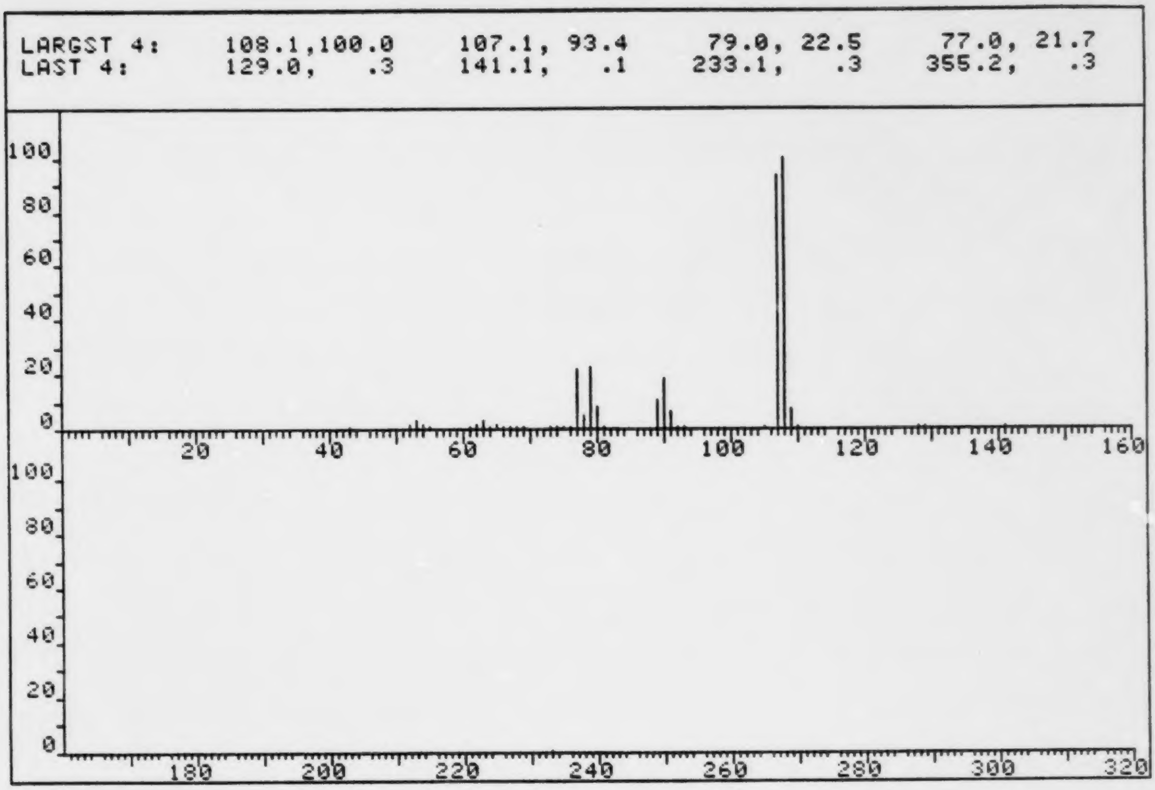


Figure B-35. Chromatogram by GC/MS for

(A) o-cresol(t_R = 5.4 min),
(B) p-chloro-m-cresol(t_R = 9.0 min),
(C) 4,6-dinitro-o-cresol(t_R = 13.3 min), and
(D) dibutyl phthalate(t_R = 17.1 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:     108.1,100.0     107.1, 93.4      79.0, 22.5      77.0, 21.7
LAST 4:       129.0,    .3    141.1,    .1    233.1,    .3    355.2,    .3
```

Figure B-36. Mass spectrum for o-cresol.

TABLE B-16. KEY IONS AND RELATIVE ABUNDANCES FOR o-CRESOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.1	.5	68.9	.3	92.0	.8
52.1	1.6	73.0	.6	93.1	.3
53.1	3.1	74.0	1.3	105.0	.6
54.0	1.7	75.0	1.0	107.1	93.4
55.0	.7	76.0	.8	108.1	100.0
61.1	.6	77.0	21.7	109.1	7.0
62.1	1.5	78.1	5.1	110.1	.6
63.0	3.1	79.0	22.5	128.0	.1
64.0	.9	80.1	7.8	129.0	.3
65.0	1.5	81.1	1.2	141.1	.1
66.0	1.0	89.1	10.3	233.1	.3
67.0	.3	90.1	18.9	355.2	.3
68.0	.6	91.1	6.4		

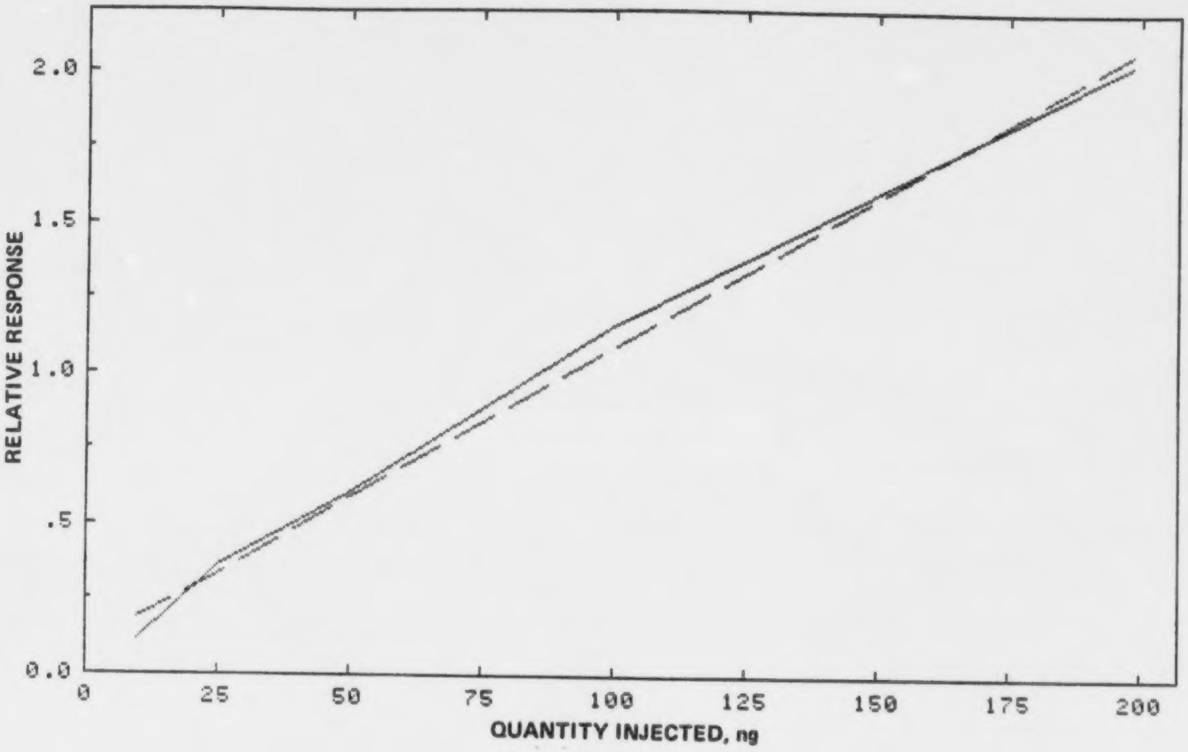
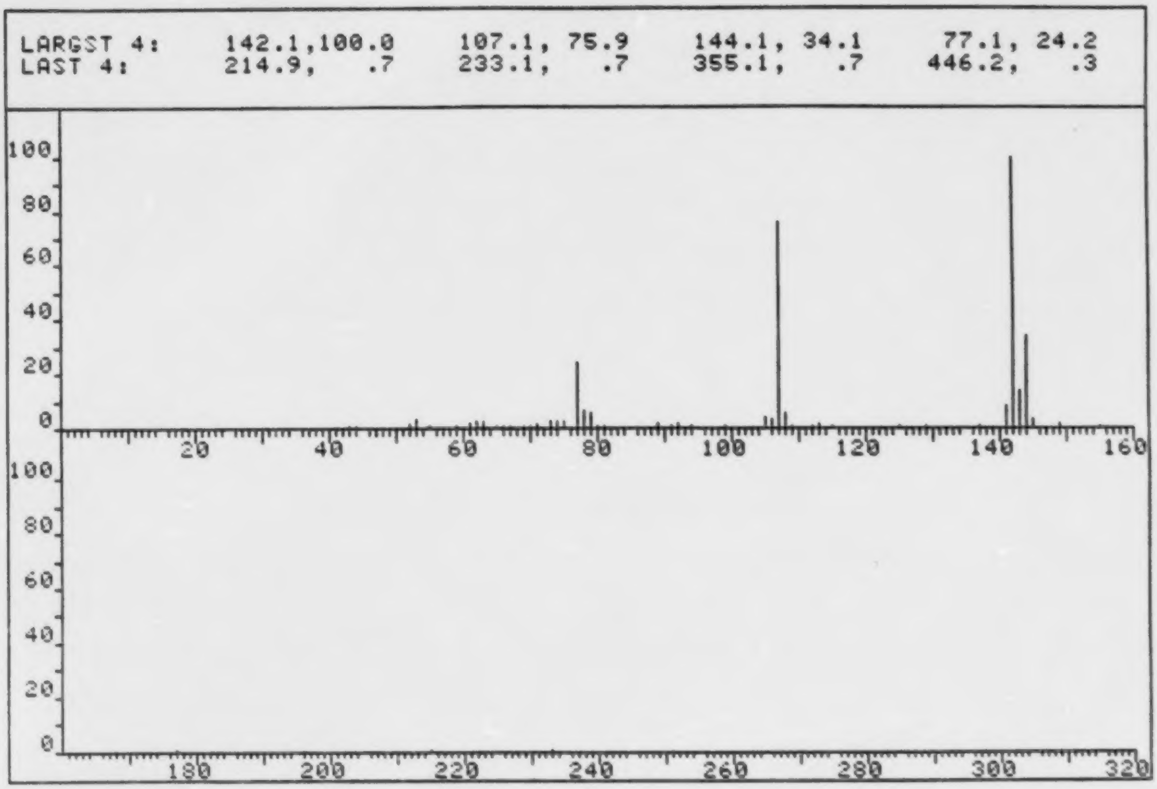


Figure B-37. Calibration curve for the determination of o-cresol by GC/MS.

Range: 9.9- 200 ng
Correlation coefficient: 0.997
Slope: 1.0×10^{-2}
y-Intercept: 8.7×10^{-2}



```
LARGST 4:     142.1,100.0     107.1, 75.9     144.1, 34.1      77.1, 24.2
LAST 4:       214.9,    .7    233.1,    .7    355.1,    .7    446.2,    .3
```

Figure B-38. Mass spectrum for p-chloro-m-cresol.

TABLE B-17. KEY IONS AND RELATIVE ABUNDANCES FOR *p*-CHLORO-*m*-CRESOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.1	.8	75.0	2.4	113.1	1.8
43.9	.1	77.1	24.2	115.1	.3
52.0	1.5	78.0	6.8	125.0	.8
53.0	3.2	79.0	5.8	129.0	1.1
55.0	.7	80.1	.7	137.1	.7
58.9	.7	81.2	.9	141.1	8.0
61.0	1.5	89.0	1.9	142.1	100.0
62.0	2.3	90.9	1.1	143.1	13.7
63.0	2.7	92.0	1.4	144.1	34.1
65.1	.7	94.1	.3	145.1	3.0
66.2	1.1	99.0	.8	149.0	1.4
67.0	.3	105.1	4.1	155.1	.7
69.0	.7	106.1	2.8	177.0	.8
70.4	1.1	107.1	75.9	214.9	.7
71.1	1.6	108.1	6.1	233.1	.7
73.0	2.4	109.0	.8	355.1	.7
74.0	2.7	112.0	.9	446.2	.3

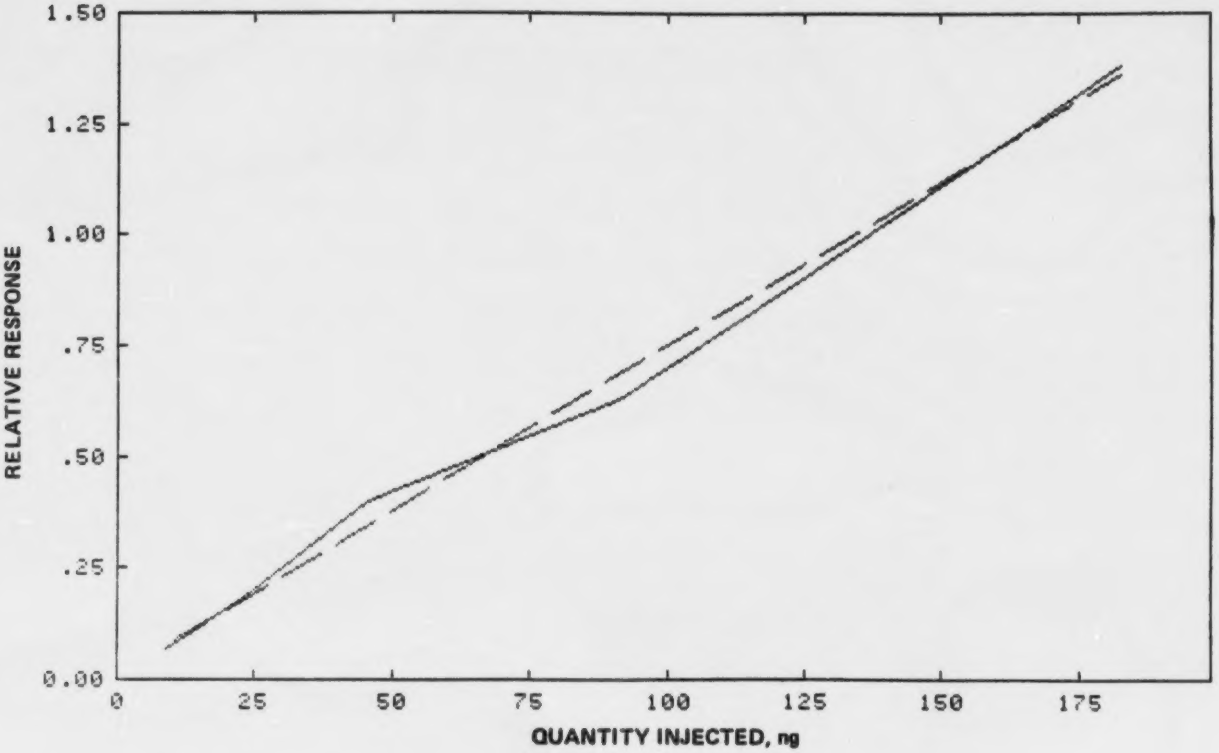
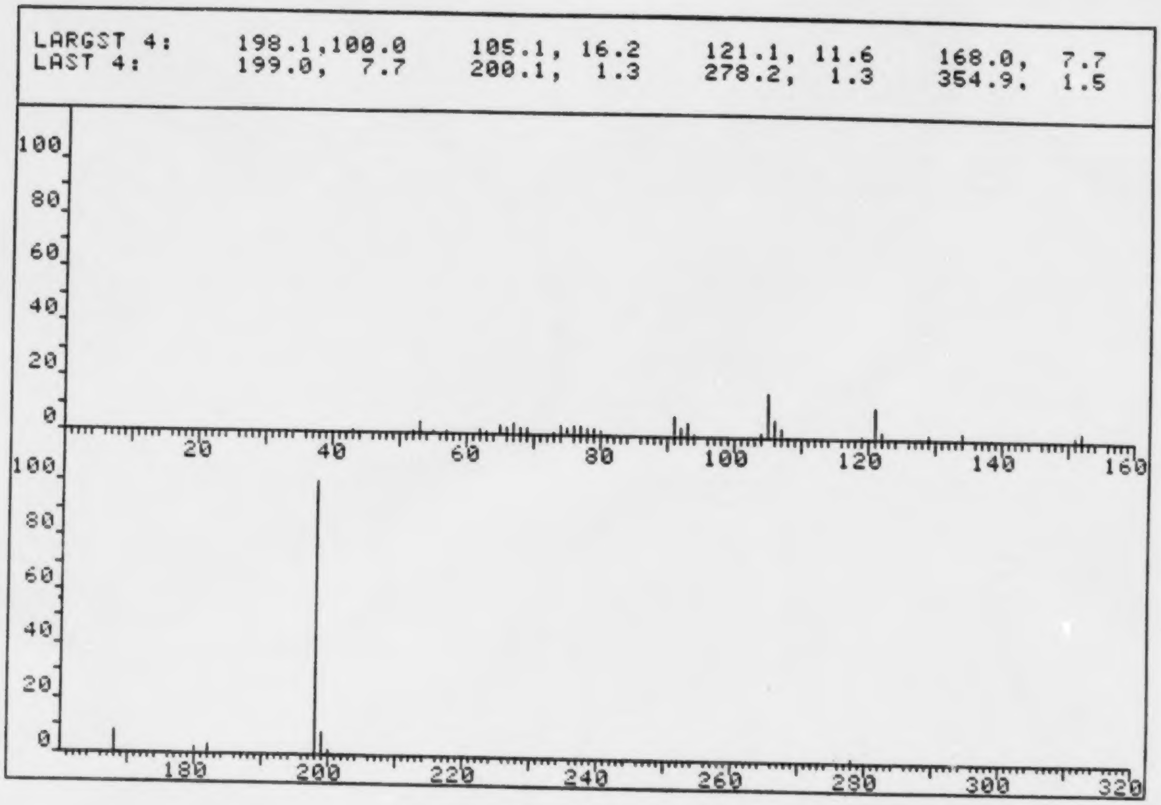


Figure B-39. Calibration curve for the determination of p-chloro-m-cresol by GC/MS.

Range: 9.1 - 180 ng
Correlation coefficient: 0.997
Slope: 7.4×10^{-3}
y-Intercept: 1.1×10^{-2}



```
LARGST 4:     198.1,100.0     105.1, 16.2     121.1, 11.6     168.0,  7.7
LAST 4:       199.0,  7.7     200.1,  1.3     278.2,  1.3     354.9,  1.5
```

Figure B-40. Mass spectrum for 4,6-dinitro-o-cresol.

TABLE B-18. KEY IONS AND RELATIVE ABUNDANCES FOR 4,6-DINITRO-*o*-CRESOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.0	1.3	76.0	3.1	121.1	11.6
52.0	1.3	77.0	2.8	122.0	2.3
53.1	4.6	78.0	2.3	129.1	1.5
54.9	.3	79.0	2.6	133.9	2.3
57.1	1.3	79.9	1.5	151.1	1.5
62.2	1.5	91.0	6.9	152.1	3.3
63.2	1.3	92.0	3.6	168.0	7.7
65.0	3.9	93.1	4.9	180.1	1.8
66.1	2.3	94.0	.3	182.0	2.6
67.0	4.4	104.0	1.5	198.1	100.0
68.0	2.1	105.1	16.2	199.0	7.7
69.0	2.1	106.0	6.4	200.1	1.3
73.0	1.3	107.1	3.6	278.2	1.3
74.0	2.8	119.2	1.3	354.9	1.5
75.2	2.6				

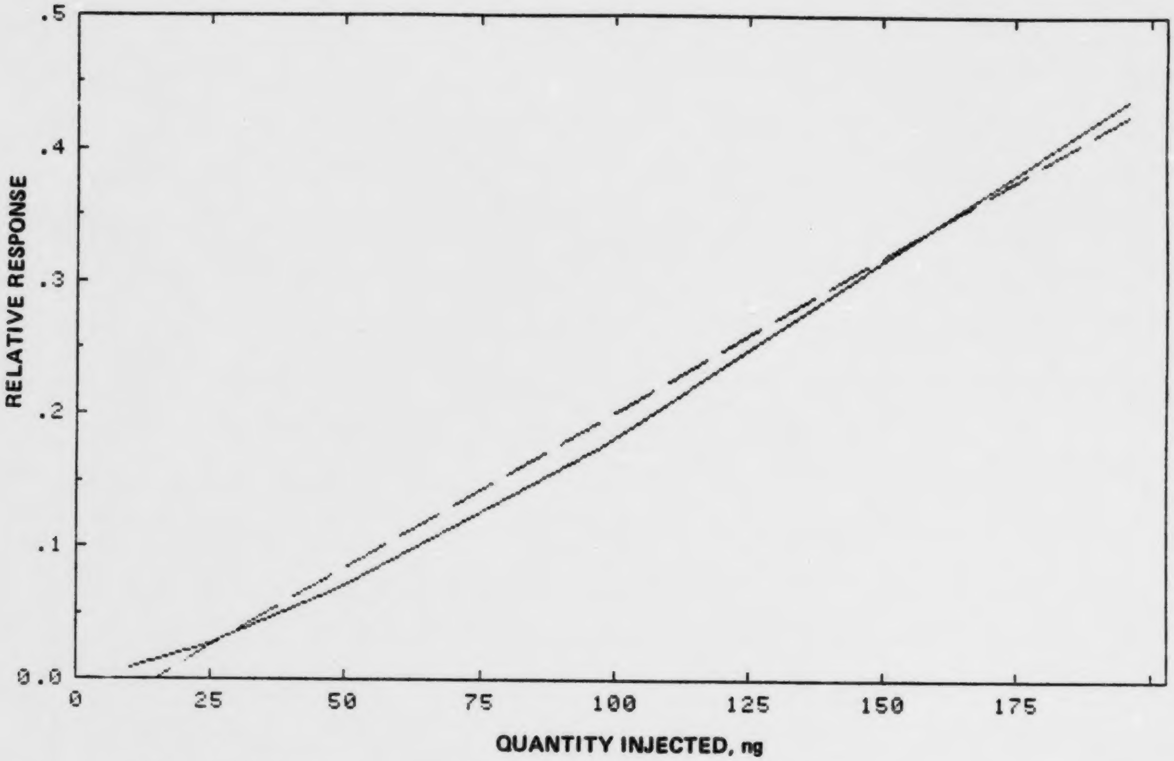
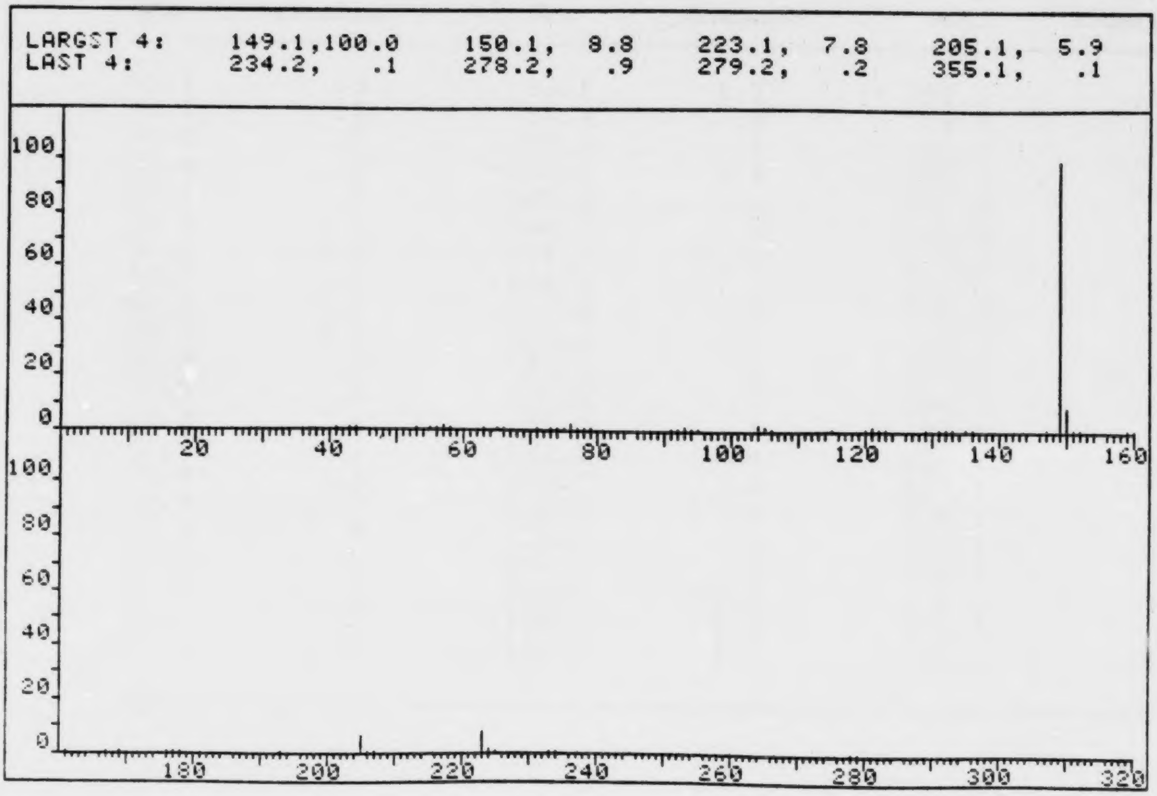


Figure B-41. Calibration curve for the determination of 4,6-dinitro-o-cresol by GC/MS.

Range: 24 - 200 ng
Correlation coefficient: 0.996
Slope: 2.3×10^{-3}
y-Intercept: -3.3×10^{-2}



```
LARGST 4:    149.1,100.0    150.1,  8.8    223.1,  7.8    205.1,  5.9
LAST 4:      234.2,    .1   278.2,   .9    279.2,   .2    355.1,    .1
```

Figure B-42. Mass spectrum for dibutyl phthalate.

TABLE B-19. KEY IONS AND RELATIVE ABUNDANCES FOR DIBUTYL PHTHALATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.1	.3	93.1	1.5	152.1	.1
43.1	.2	94.1	.0	158.9	.1
44.0	.0	95.0	.1	160.1	.7
53.0	.2	104.1	2.4	161.1	.2
55.1	.3	105.0	1.6	167.0	.5
56.0	1.2	106.0	.3	169.0	.1
57.1	1.3	115.0	.0	176.0	.1
58.6	.1	120.2	.1	177.0	.1
63.1	.1	121.0	1.5	178.0	.1
65.0	1.2	122.0	1.1	193.1	.1
66.2	.2	123.1	.6	205.1	5.9
71.0	.1	129.0	.2	206.1	.8
73.2	.4	131.0	.1	207.1	.2
73.9	.2	132.1	.4	223.1	7.8
75.0	.3	133.1	.2	224.1	1.0
76.0	2.3	135.1	.4	225.1	.2
77.0	.4	136.0	.2	233.1	.2
78.1	.1	147.1	.3	234.2	.1
79.1	.1	149.1	100.0	278.2	.9
91.1	.7	150.1	8.8	279.2	.2
92.1	.5	151.1	1.1	355.1	.1

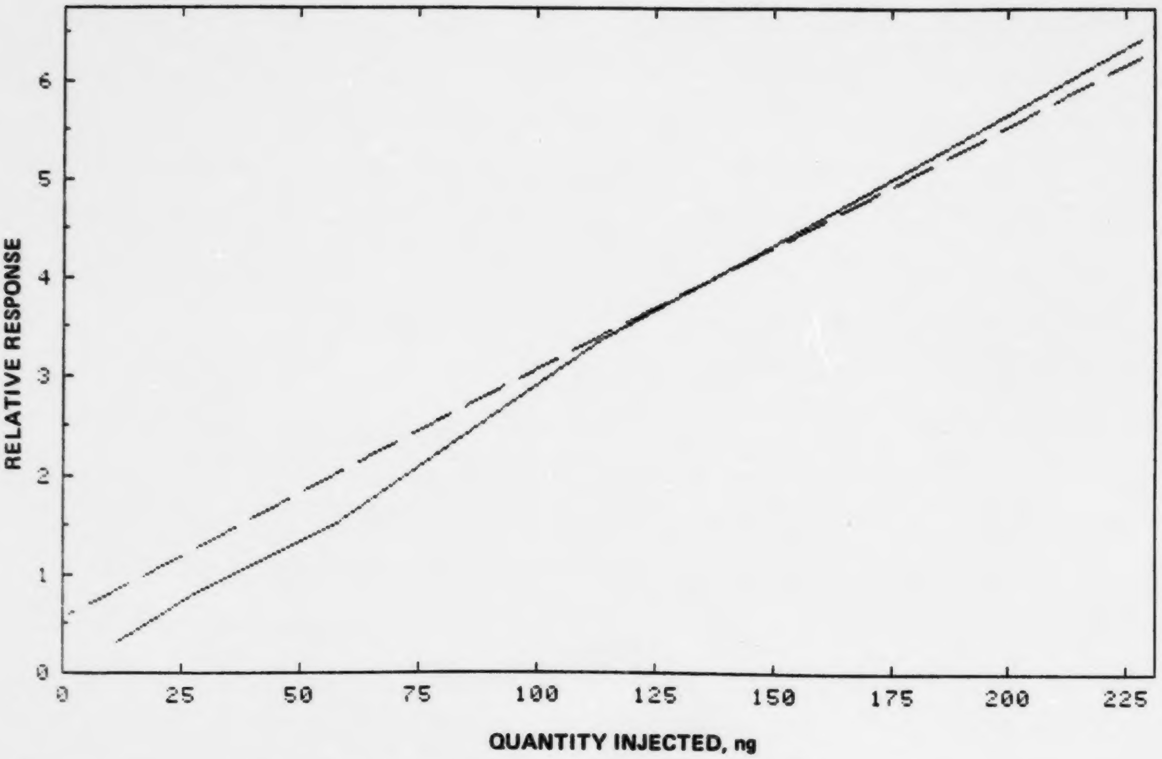


Figure B-43. Calibration curve for the determination of dibutyl phthalate by GC/MS.

Range: 28 - 230
Correlation coefficient: 0.982
Slope: 2.6×10^{-2}
y-Intercept: 4.4×10^{-1}

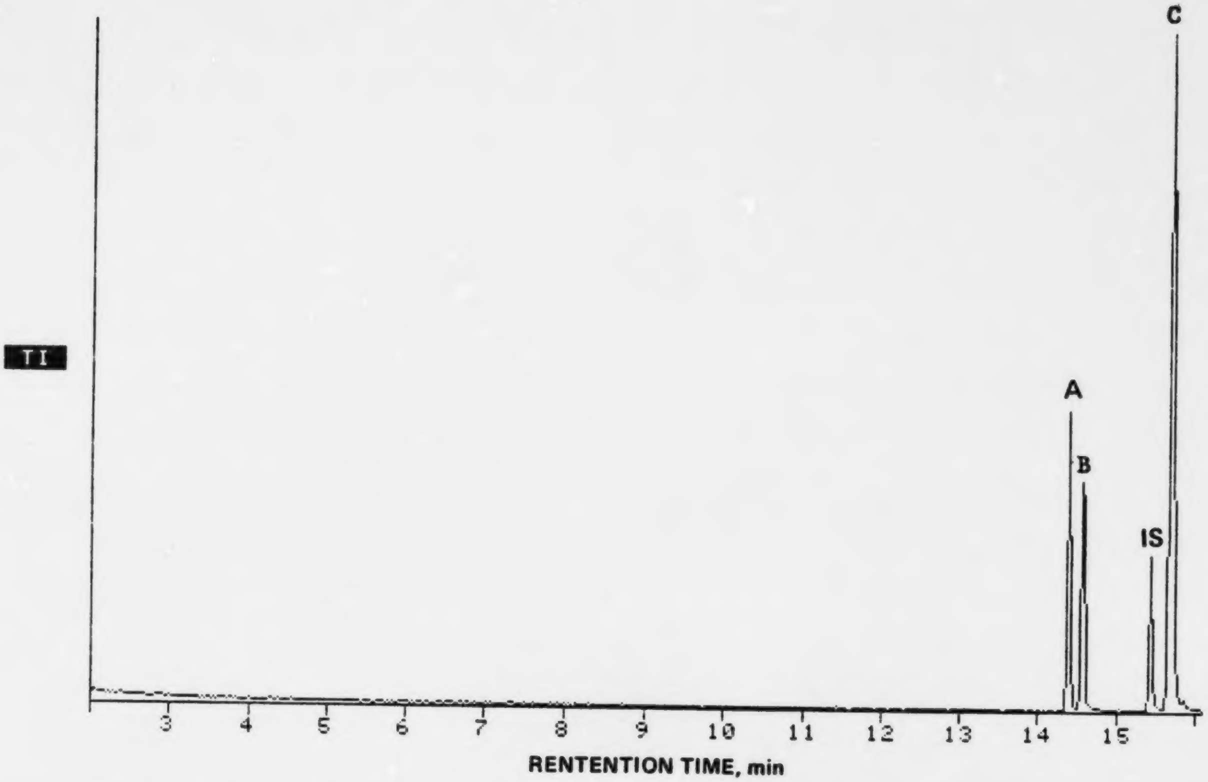
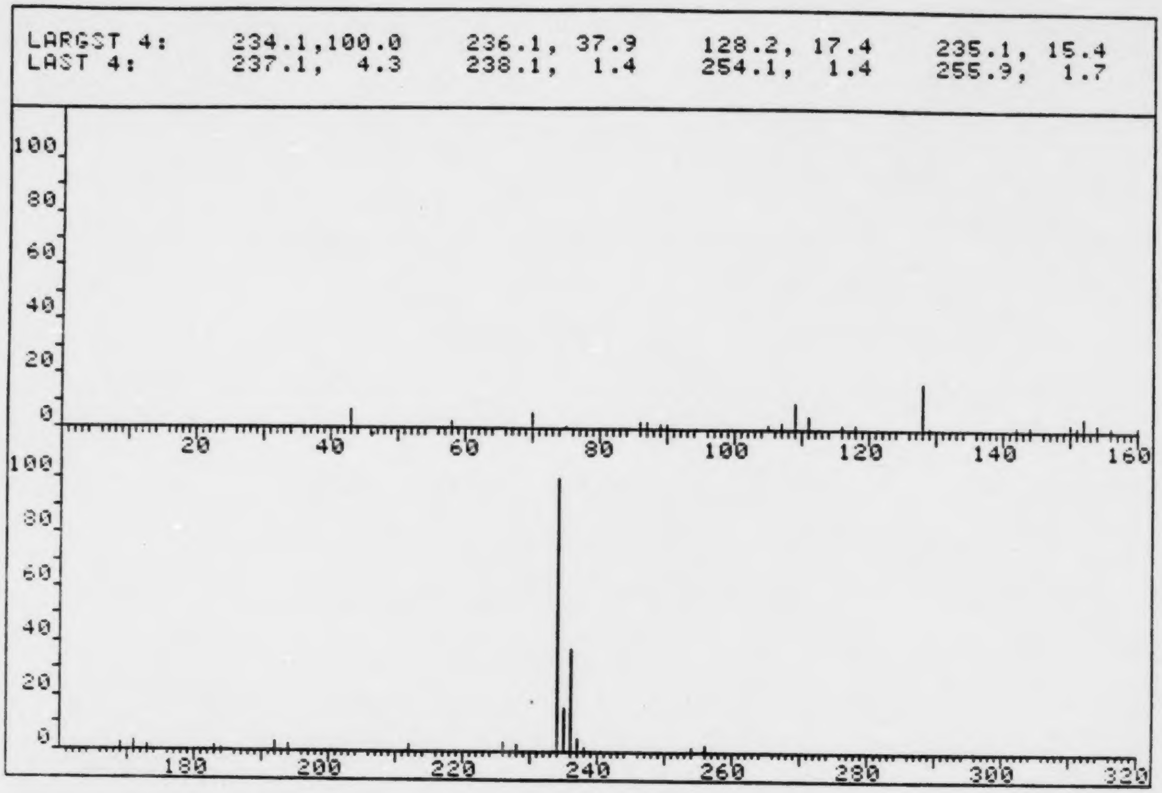


Figure B-44. Chromatogram by GC/MS for

(A) diallate isomer(t_R = 14.3 min),
(B) diallate isomer(t_R = 14.6 min), and
(C) disulfoton(t_R = 15.6 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:      234.1,100.0     236.1, 37.9     128.2, 17.4     235.1, 15.4
LAST 4:        237.1,   4.3    238.1,  1.4     254.1,   1.4    255.9,  1.7
```

Figure B-45. Mass spectrum for diallate.

TABLE B-20. KEY IONS AND RELATIVE ABUNDANCES FOR DIALLATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.2	6.8	128.2	17.4	184.1	.6
58.1	2.3	129.1	.6	192.1	3.4
70.1	5.4	142.1	1.7	194.0	2.0
75.1	.6	144.1	1.4	212.0	1.7
86.1	2.6	150.1	2.3	226.1	3.1
87.1	2.6	151.0	1.4	228.1	2.0
89.0	1.4	152.1	4.8	234.1	100.0
90.1	1.4	154.0	2.6	235.1	15.4
105.0	1.7	155.9	2.0	236.1	37.9
107.0	2.3	160.1	1.4	237.1	4.3
109.0	9.7	169.0	1.7	238.1	1.4
111.0	5.1	171.1	3.1	254.1	1.4
116.1	1.4	173.2	1.4	255.9	1.7
118.2	2.0	183.1	1.4		

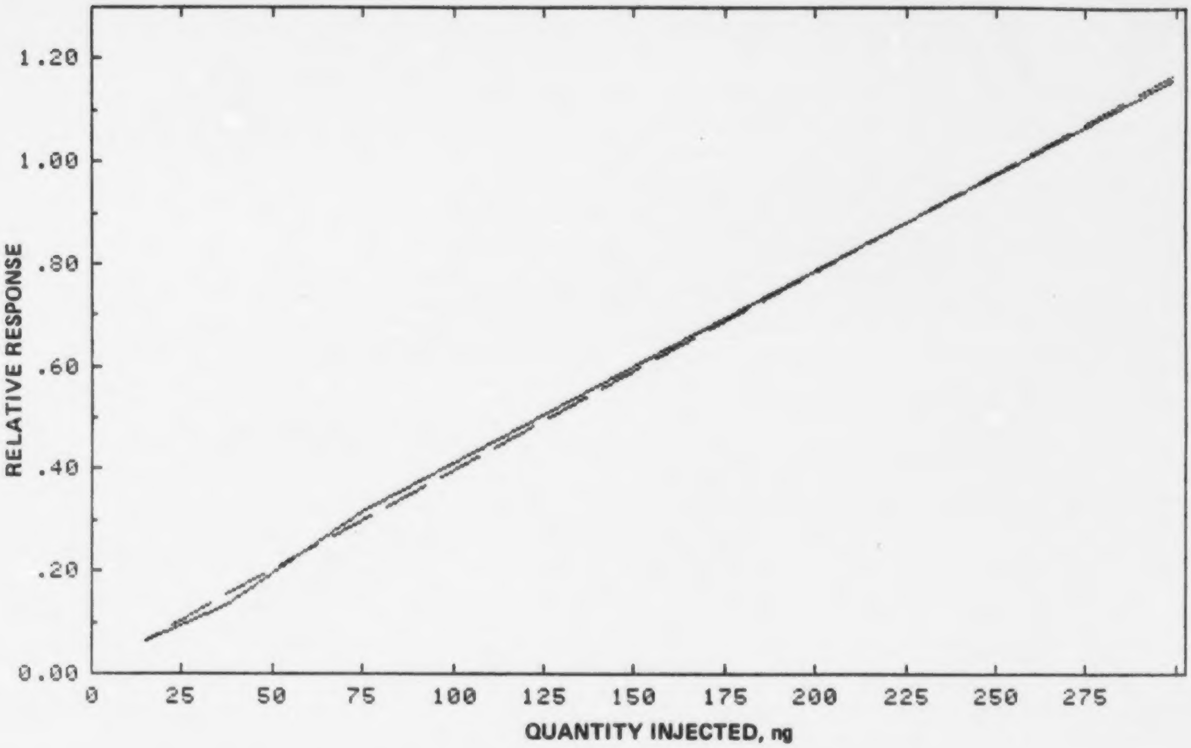


Figure B-46. Calibration curve for the determination of diallate by GC/MS.

Range: 15 - 300 ng
Correlation coefficient: 0.999
Slope: 3.9×10^{-3}
y-Intercept: 7.6×10^{-3}

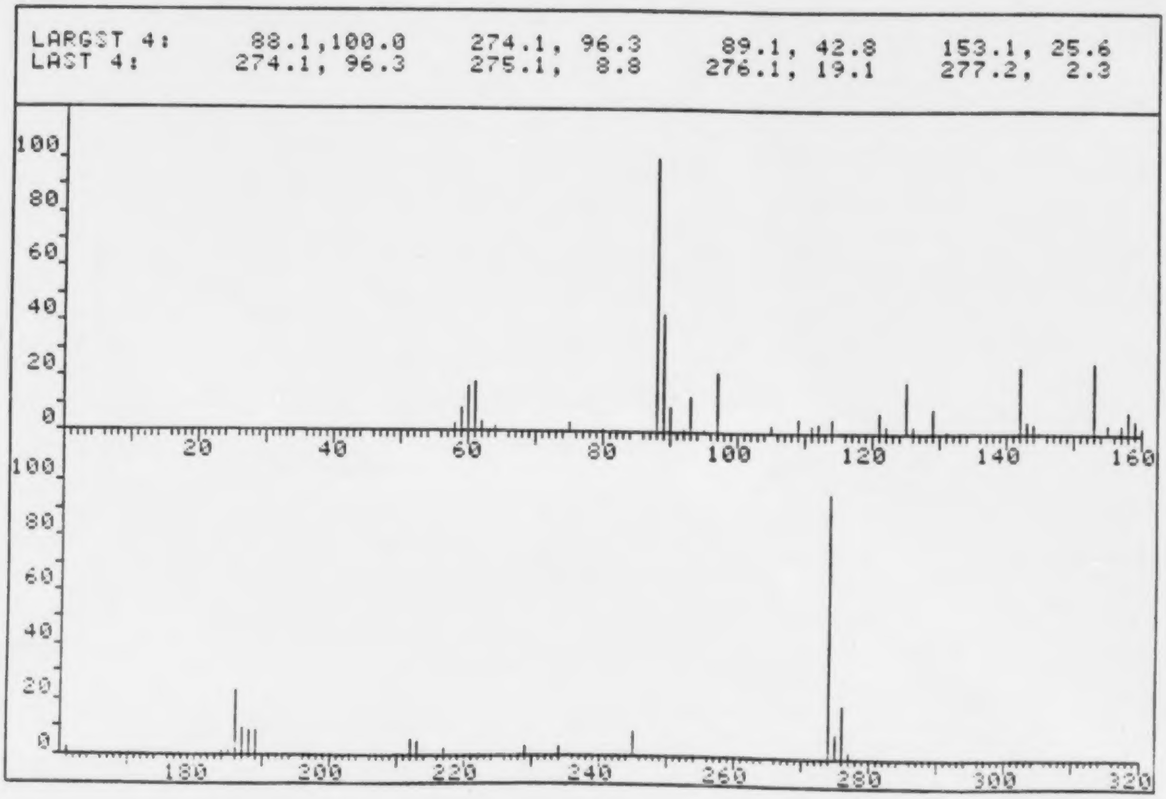


Figure B-47. Mass spectrum for disulfoton.

TABLE B-21. KEY IONS AND RELATIVE ABUNDANCES FOR DISULFOTON

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
58.1	2.3	112.0	2.8	160.9	2.3
59.1	8.4	114.0	4.7	184.0	.9
60.1	16.3	121.1	7.0	185.0	2.3
61.1	18.1	122.1	2.3	186.1	23.3
62.2	3.7	125.0	18.6	187.1	9.3
64.1	1.4	126.2	2.3	188.2	8.4
75.1	2.8	129.1	8.8	189.0	8.8
80.2	.9	131.0	.5	212.1	5.1
88.1	100.0	142.1	24.2	213.1	4.7
89.1	42.8	143.0	4.2	217.0	2.8
90.1	9.3	143.9	3.3	229.0	3.3
92.1	.9	153.1	25.6	234.0	2.8
93.1	13.5	155.1	3.3	245.0	8.4
94.9	.9	157.0	3.3	274.1	96.3
97.0	22.3	158.0	7.9	275.1	8.8
105.0	2.3	159.1	4.7	276.1	19.1
109.0	5.1	160.0	2.3	277.2	2.3
111.0	2.3				

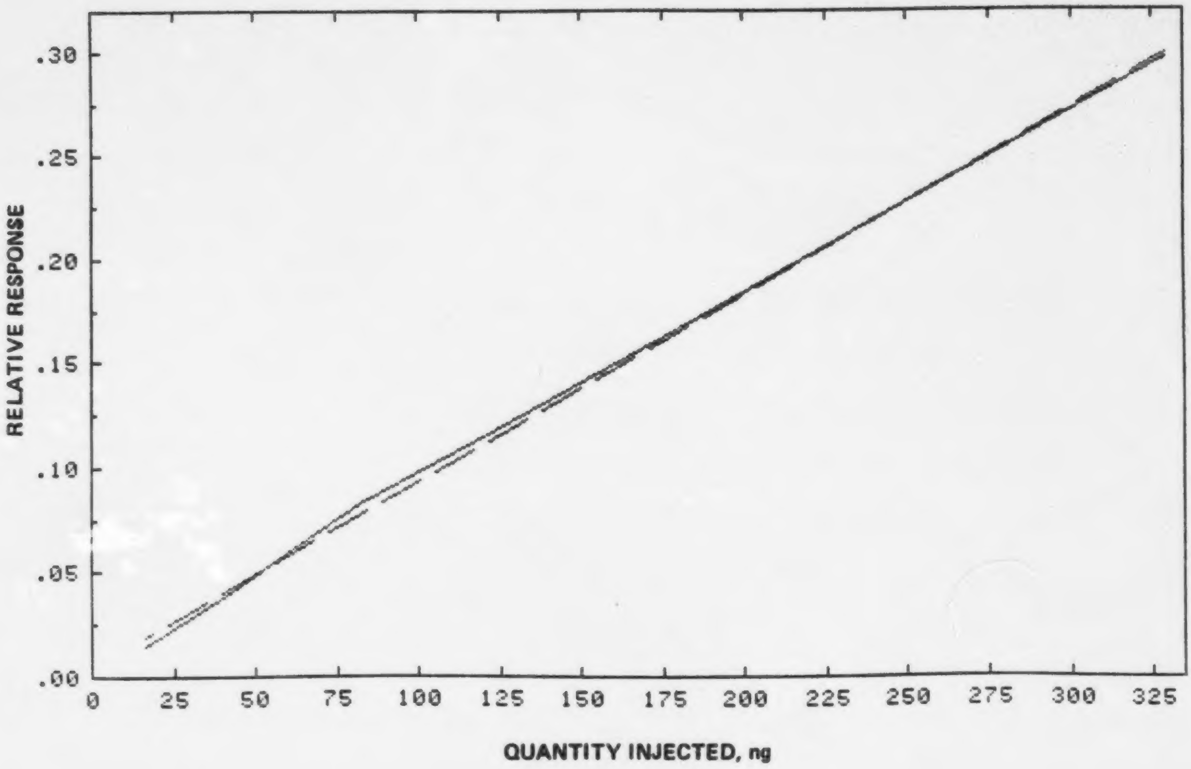


Figure B-48. Calibration curve for the determination of disulfoton by GC/MS.

Range: 16 - 330 ng
Correlation coefficient: 0.999
Slope: 9.0×10^{-4}
y-Intercept: 4.1×10^{-3}

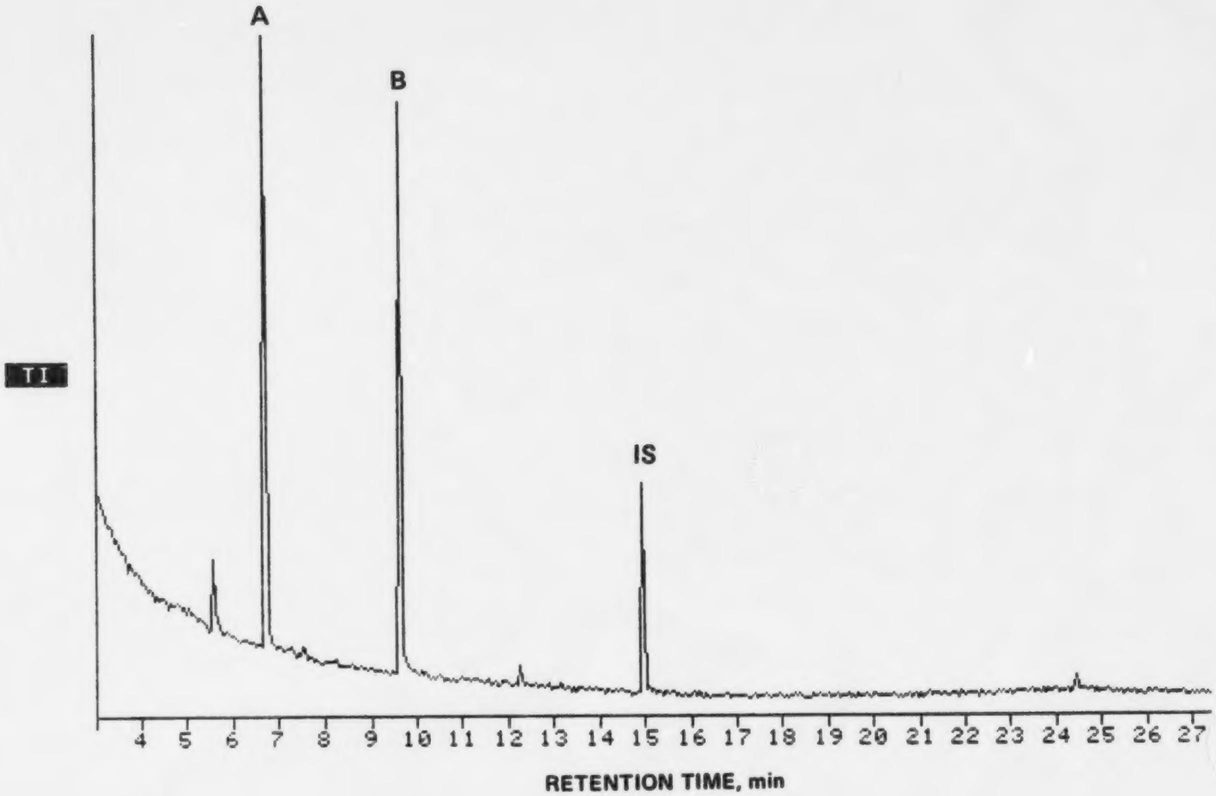
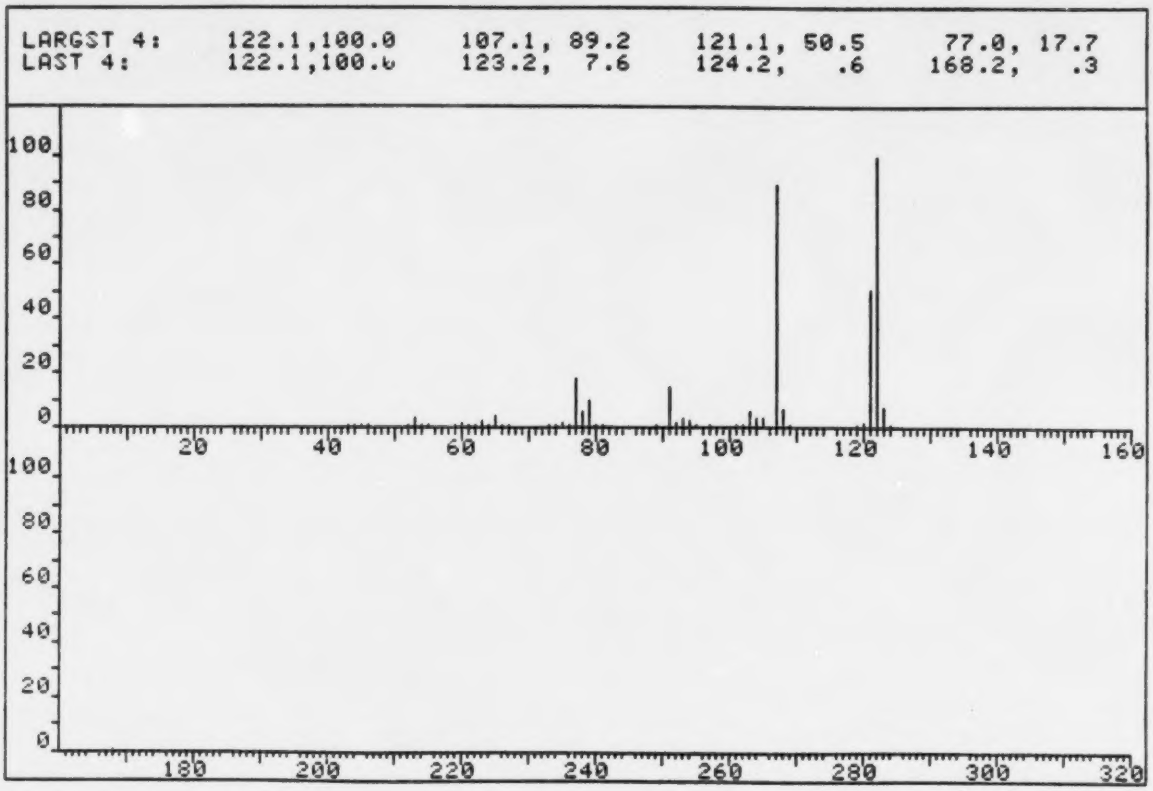


Figure B-49. Chromatogram by GC/MS for

(A) 2,4-dimethylphenol(t_R = 6.9 min) and
(B) 2,4,6-trichlorophenol(t_R = 9.9 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:      122.1,100.0     107.1, 89.2     121.1, 50.5      77.0, 17.7
LAST 4:        122.1,100.0     123.2,  7.6     124.2,    .6    168.2,    .3
```

Figure B-50. Mass spectrum for 2,4-dimethylphenol.

TABLE B-22. KEY IONS AND RELATIVE ABUNDANCES FOR 2,4-DIMETHYLPHENOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.0	.7	67.2	.8	97.0	.5
44.1	.8	73.1	.6	101.1	.5
45.2	.9	74.0	1.2	102.1	1.1
46.1	.5	75.0	1.3	103.1	5.6
52.0	.9	76.2	.2	104.1	3.7
53.0	3.4	77.0	17.7	105.1	3.4
54.0	.5	78.0	5.8	107.1	89.2
55.1	.6	79.1	10.1	108.1	6.4
55.6	.5	80.1	1.2	109.2	.6
59.0	.9	81.1	.7	119.0	1.1
59.9	1.9	89.1	1.1	120.1	1.6
61.0	.8	91.1	15.0	121.1	50.5
62.0	1.1	92.1	2.0	122.1	100.0
63.0	2.4	93.1	3.4	123.2	7.6
64.0	1.1	94.1	2.1	124.2	.6
65.0	4.2	95.1	.6	168.2	.3
66.0	1.2				

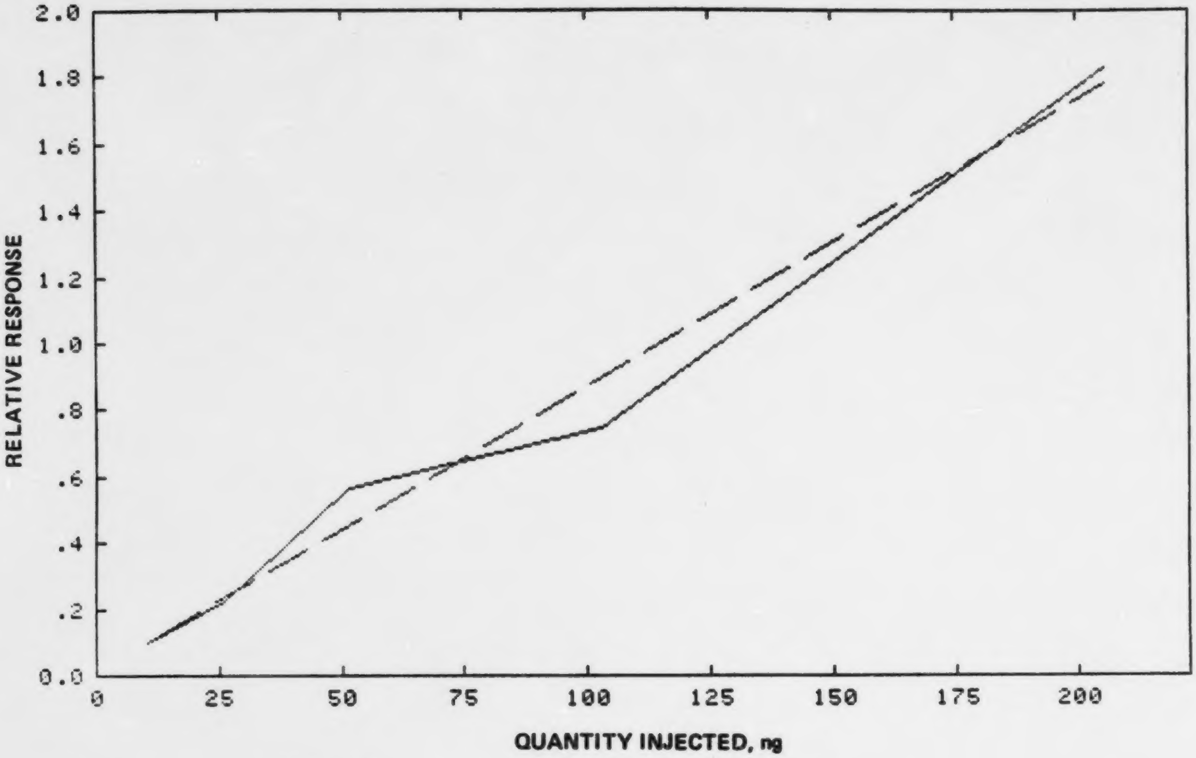
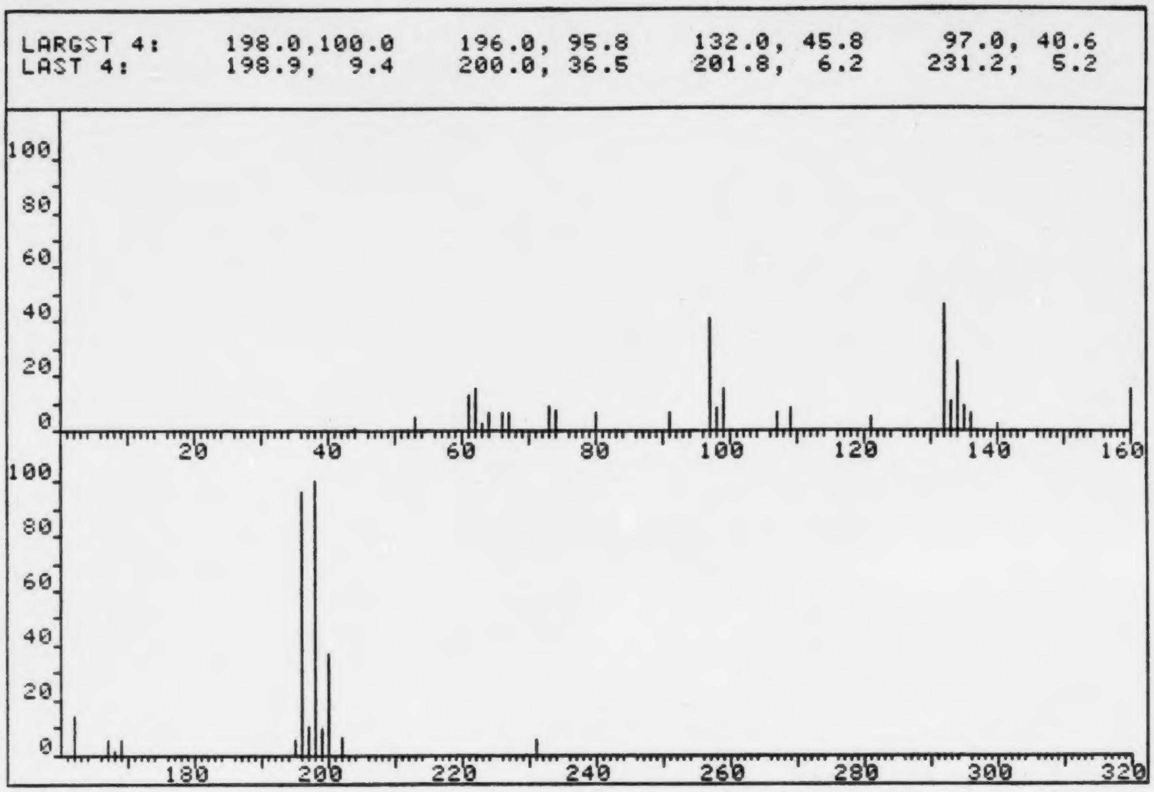


Figure B-51. Calibration curve for the determination of 2,4-dimethylphenol by GC/MS.

Range: 10 - 210 ng
Correlation coefficient: 0.990
Slope: 8.6×10^{-3}
y-Intercept: 1.2×10^{-2}



```
LARGST 4:    198.0,100.0    196.0, 95.8    132.0, 45.8     97.0, 40.6
LAST 4:      198.9,  9.4    200.0, 36.5    201.8,  6.2    231.2,  5.2
```

Figure B-52. Mass spectrum for 2,4,6-trichlorophenol.

TABLE B-23. KEY IONS AND RELATIVE ABUNDANCES FOR 2,4,6-TRICHLOROPHENOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
44.1	1.0	91.0	6.2	160.0	15.6
52.8	5.2	97.0	40.6	162.0	14.6
61.0	12.5	98.0	8.3	166.9	5.2
62.0	15.6	99.0	15.6	168.1	1.0
62.9	2.1	107.0	6.2	169.0	5.2
64.0	6.2	109.1	8.3	195.1	5.2
66.0	1.0	121.4	5.2	196.0	95.8
66.3	6.2	132.0	45.8	197.1	10.4
66.7	6.2	133.0	10.4	198.0	100.0
67.0	6.2	134.0	25.0	198.9	9.4
73.2	9.4	134.9	9.4	200.0	36.5
74.0	7.3	136.0	6.2	201.8	6.2
79.9	6.2	140.0	2.1	231.2	5.2

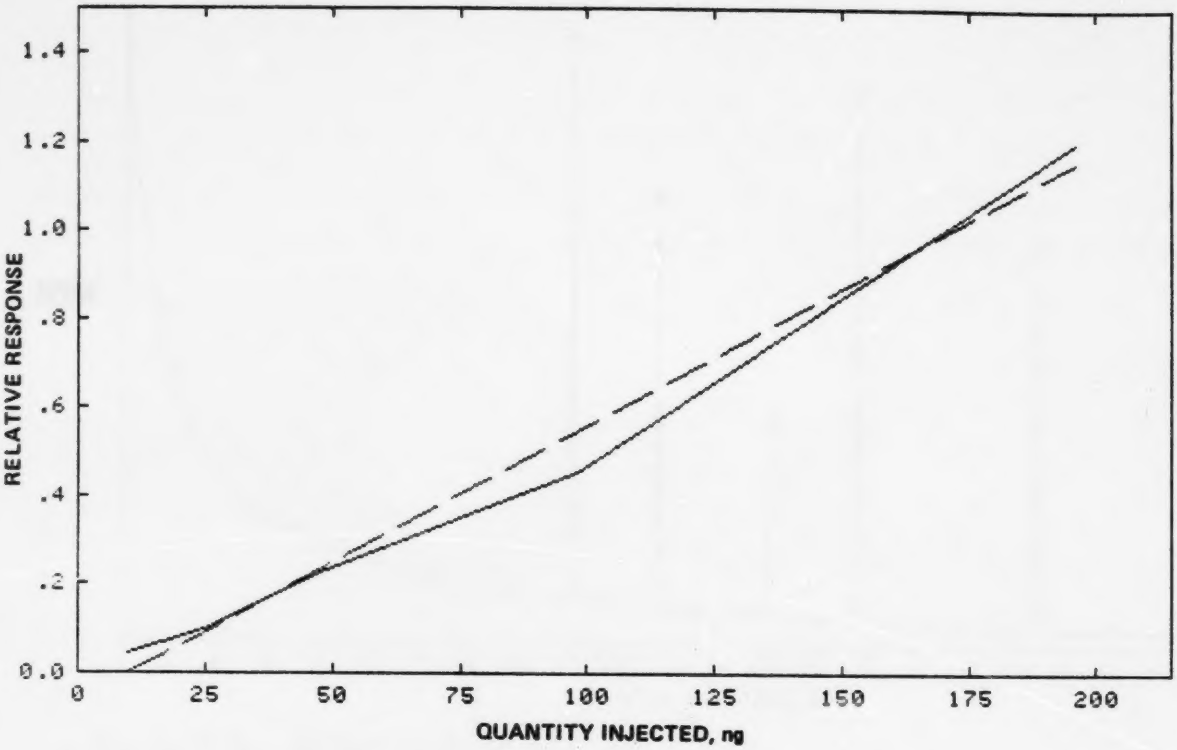


Figure B-53. Calibration curve for the determination of 2,4,6-trichlorophenol by GC/MS.

Range: 24 - 200 ng
Correlation coefficient: 0.992
Slope: 6.2×10^{-3}
y-Intercept: -6.3×10^{-2}

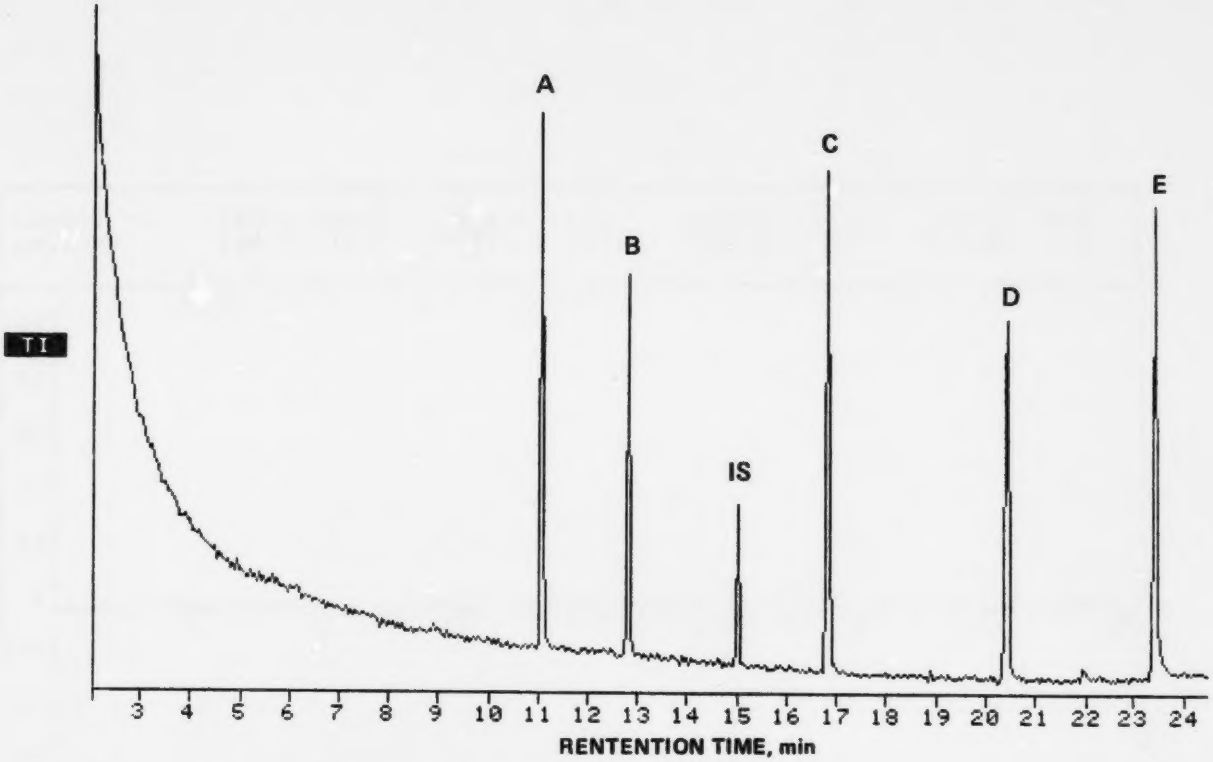
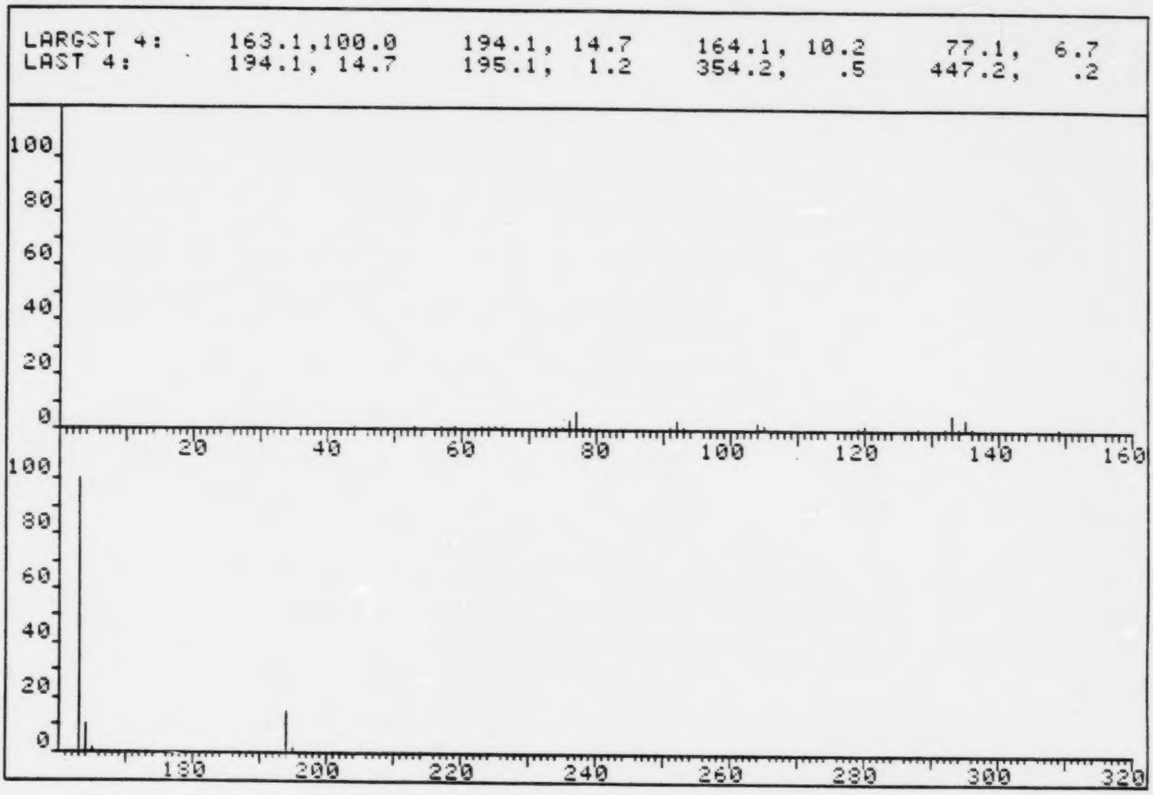


Figure B-54. Chromatogram by GC/MS for

(A) dimethyl phthalate(t_R = 11.1 min),
(B) diethyl phthalate(t_R = 13.1 min),
(C) diisobutyl phthalate(t_R = 17.1 min),
(D) butylbenzyl phthalate(t_R = 20.8 min), and
(E) dioctyl phthalate(t_R = 23.5 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:     163.1,100.0     194.1, 14.7     164.1, 10.2      77.1,  6.7
LAST 4:       194.1, 14.7     195.1,  1.2     354.2,    .5    447.2,    .2
```

Figure B-55. Mass spectrum for dimethyl phthalate.

TABLE B-24. KEY IONS AND RELATIVE ABUNDANCES FOR DIMETHYL PHTHALATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
44.0	.5	77.1	6.7	133.1	5.8
52.8	.9	77.9	.2	134.1	.7
56.9	.7	79.0	.9	135.0	4.2
59.0	.7	91.2	.7	136.0	.5
62.9	.2	92.1	3.5	149.1	.7
64.1	1.2	92.7	.5	163.1	100.0
65.0	.7	104.1	2.6	164.1	10.2
66.1	.5	105.0	1.6	165.1	1.2
73.0	.5	119.1	.5	194.1	14.7
74.0	.7	120.0	1.9	195.1	1.2
75.0	.9	128.2	.5	354.2	.5
76.0	3.7	132.1	.7	447.2	.2

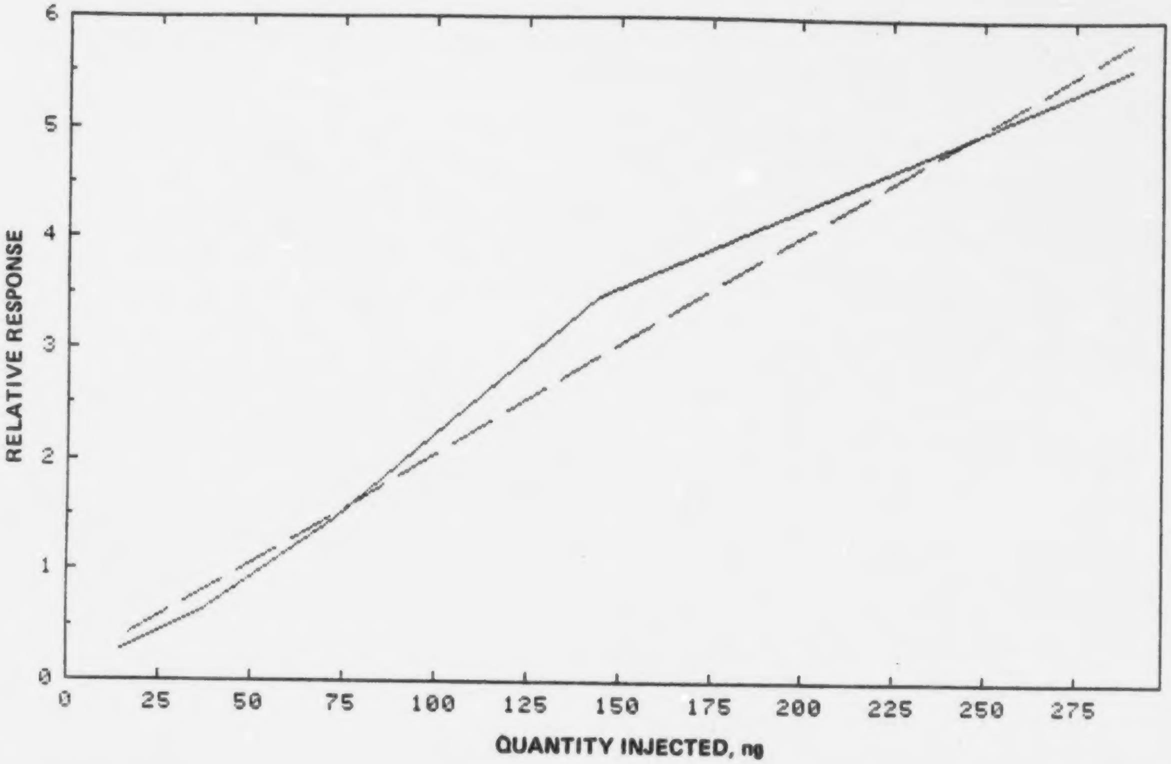
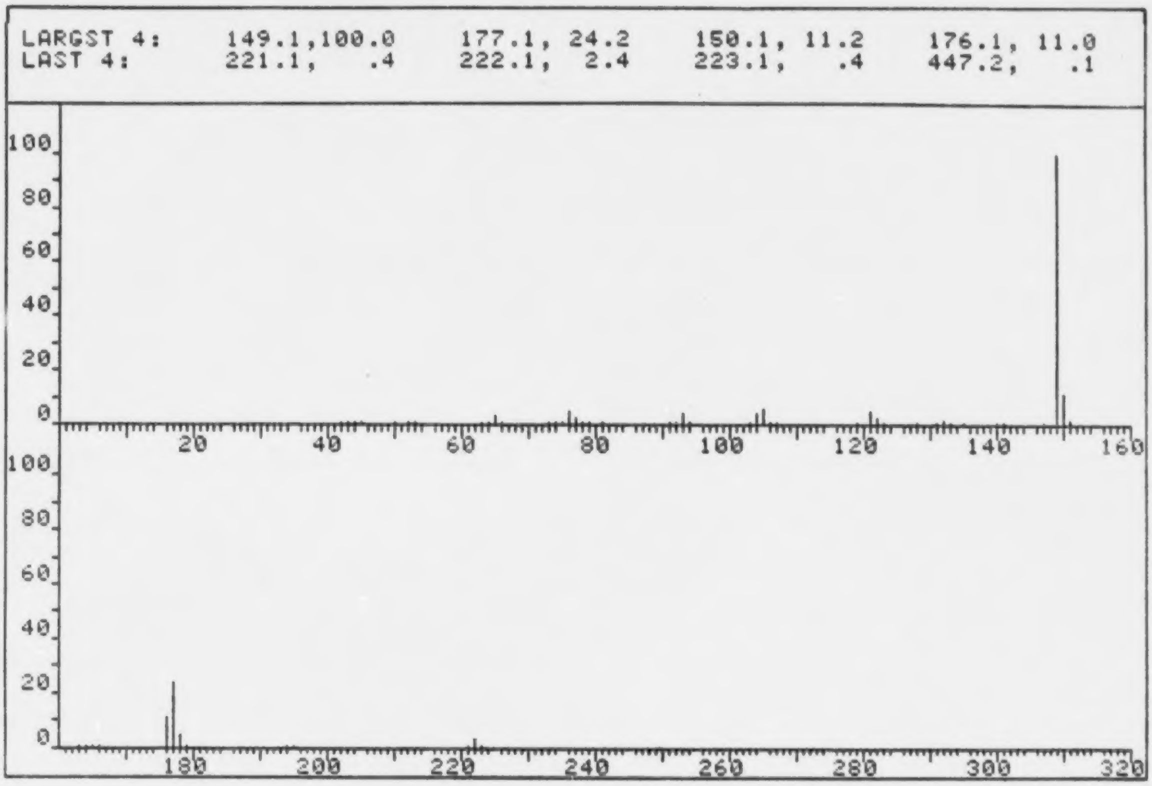


Figure B-56. Calibration curve for the determination of dimethyl phthalate by GC/MS.

Range: 14 - 290 ng
Correlation coefficient: 0.990
Slope: 2.0×10^{-2}
y-Intercept: 8.1×10^{-2}



```
LARGST 4:    149.1,100.0    177.1, 24.2    150.1, 11.2    176.1, 11.0
LAST 4:      221.1,    .4   222.1,  2.4    223.1,    .4   447.2,    .1
```

Figure B-57. Mass spectrum for diethyl phthalate.

TABLE B-25. KEY IONS AND RELATIVE ABUNDANCES FOR DIETHYL PHTHALATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.8	.4	91.9	.4	141.1	.2
43.1	.8	93.1	4.6	147.1	.3
44.1	.6	94.1	.4	149.1	100.0
45.2	.6	102.9	.3	150.1	11.2
50.0	.1	103.1	.2	151.1	1.3
52.0	.8	104.1	4.4	163.0	.3
52.9	.6	105.1	6.0	164.1	.4
63.0	.2	106.1	1.3	165.1	.3
64.0	.4	107.1	.2	166.1	.2
65.1	3.2	119.0	.2	176.1	11.0
66.1	.9	121.0	5.0	177.1	24.2
73.0	.2	122.0	2.5	178.1	4.9
74.0	.4	123.2	.2	179.1	.5
75.0	.8	128.1	.3	194.2	.2
76.0	4.9	131.0	.3	195.1	.2
77.0	2.1	132.1	1.7	221.1	.4
78.0	.1	133.0	.4	222.1	2.4
79.0	.2	135.0	.8	223.1	.4
81.2	.2	140.2	.2	447.2	.1
91.1	.4				

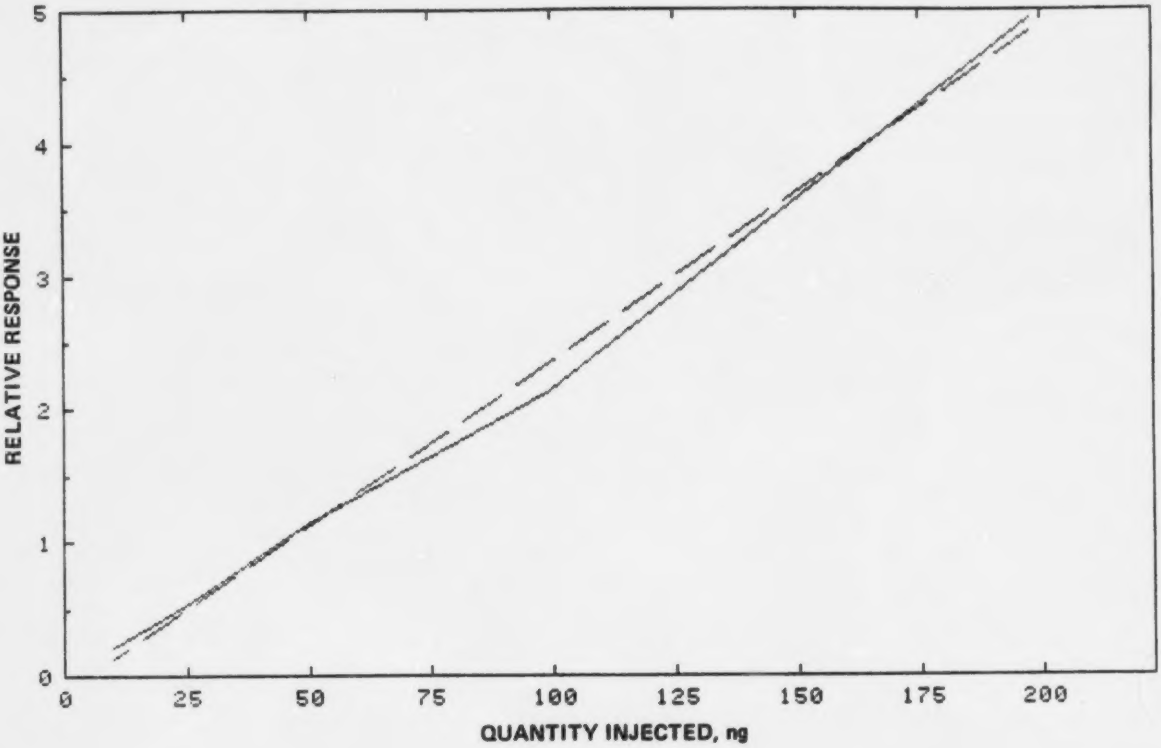
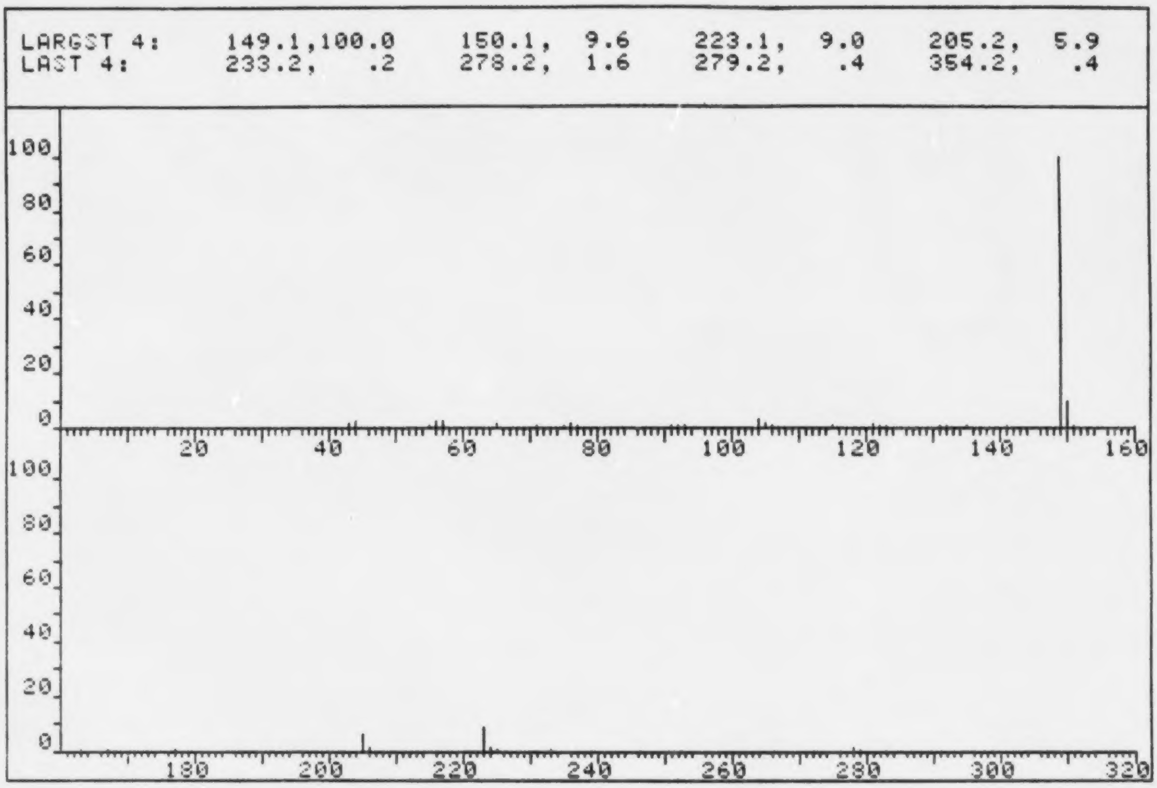


Figure B-58. Calibration curve for the determination of diethyl phthalate by GC/MS.

Range: 25 - 200 ng
Correlation coefficient: 0.998
Slope: 2.5×10^{-2}
y-Intercept: -1.2×10^{-1}



```
LARGST 4:     149.1,100.0     150.1,  9.6     223.1,  9.0     205.2,  5.9
LAST 4:       233.2,   .2     278.2,  1.6     279.2,   .4     354.2,   .4
```

Figure B-59. Mass spectrum for diisobutyl phthalate.

TABLE B-26. KEY IONS AND RELATIVE ABUNDANCES FOR DIISOBUTYL PHTHALATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.1	1.8	105.1	2.0	160.1	.6
44.0	2.2	106.0	.4	163.2	.2
55.0	1.0	115.0	.4	167.0	.4
56.1	2.2	121.1	1.8	177.0	.2
57.1	2.2	122.0	1.0	205.2	5.9
65.1	1.4	123.0	.8	206.1	1.0
71.0	.4	130.9	.4	223.1	9.0
75.1	.6	132.0	.6	224.1	1.4
76.1	2.0	135.1	.6	225.1	.2
77.0	.4	141.1	.4	233.2	.2
91.2	.4	149.1	100.0	278.2	1.6
92.1	.4	150.1	9.6	279.2	.4
92.9	1.2	151.1	.8	354.2	.4
104.1	3.1				

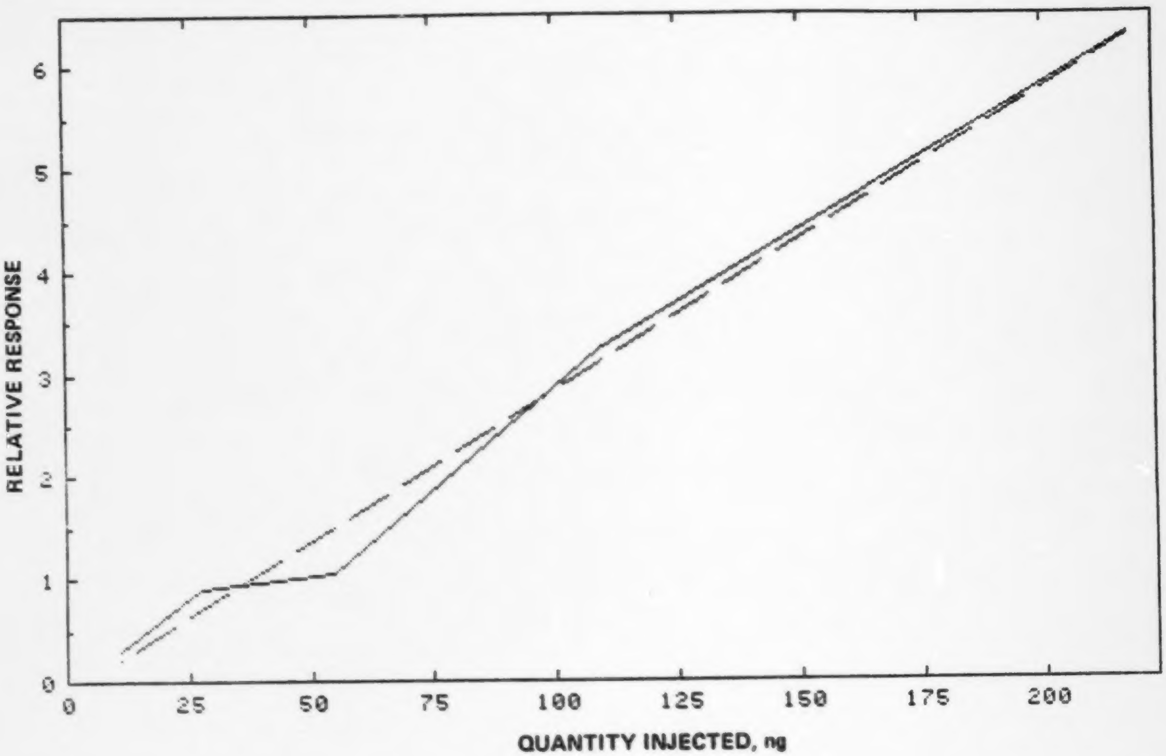
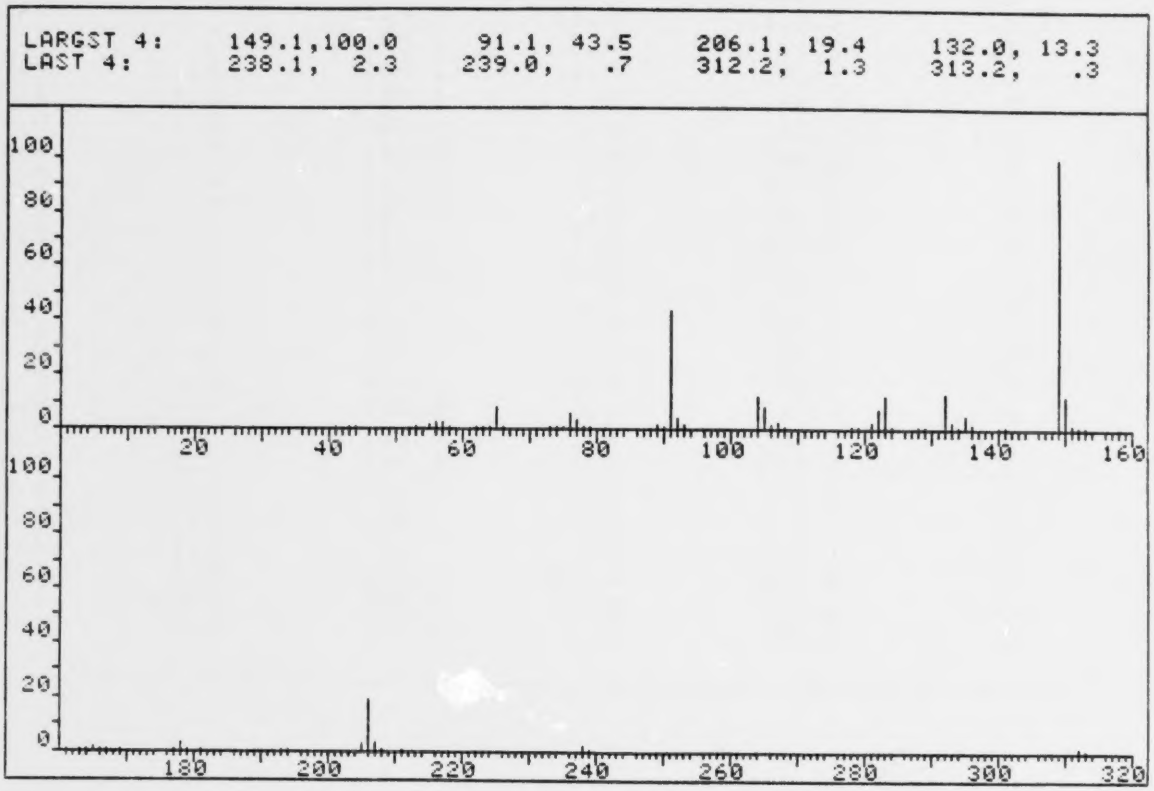


Figure B-60. Calibration curve for the determination of diisobutyl phthalate by GC/MS.

Range: 27 - 220 ng
Correlation coefficient: 0.994
Slope: 2.9×10^{-2}
y-Intercept: -1.0×10^{-1}



```
LARGST 4:    149.1,100.0     91.1, 43.5    206.1, 19.4    132.0, 13.3
LAST 4:      238.1,  2.3    239.0,   .7    312.2,  1.3    313.2,   .3
```

Figure B-61. Mass spectrum for butylbenzyl phthalate.

TABLE B-27. KEY IONS AND RELATIVE ABUNDANCES FOR BUTYLBENZENE PHTHALATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.1	.3	93.0	1.9	152.1	.4
42.9	.9	104.0	11.7	153.1	.3
44.0	.7	105.1	8.4	161.1	.3
53.0	.6	106.1	1.9	163.1	.3
55.1	1.6	107.1	2.6	164.1	.3
56.0	2.5	108.1	.6	165.1	1.0
57.1	2.5	118.0	.3	166.2	.4
58.0	.4	119.5	1.2	167.1	.4
61.8	.3	121.2	2.2	169.2	.3
63.0	1.2	122.1	7.5	177.2	.9
64.1	.7	123.1	12.0	178.2	2.9
65.1	7.6	124.2	1.2	179.1	.3
66.0	.6	128.0	.4	181.2	.1
73.0	.4	129.0	.3	193.1	.3
74.0	.1	132.0	13.3	194.1	.4
75.0	.7	133.2	2.6	205.1	2.9
76.0	5.6	134.0	.4	206.1	19.4
77.0	3.7	135.0	5.3	207.1	3.1
78.2	.6	136.1	1.6	208.1	.3
79.0	1.2	140.1	.3	211.1	.3
89.1	1.9	141.2	.3	238.1	2.3
90.1	1.2	149.1	100.0	239.0	.7
91.1	43.5	150.1	12.0	312.2	1.3
92.1	4.5	151.0	1.5	313.2	.3

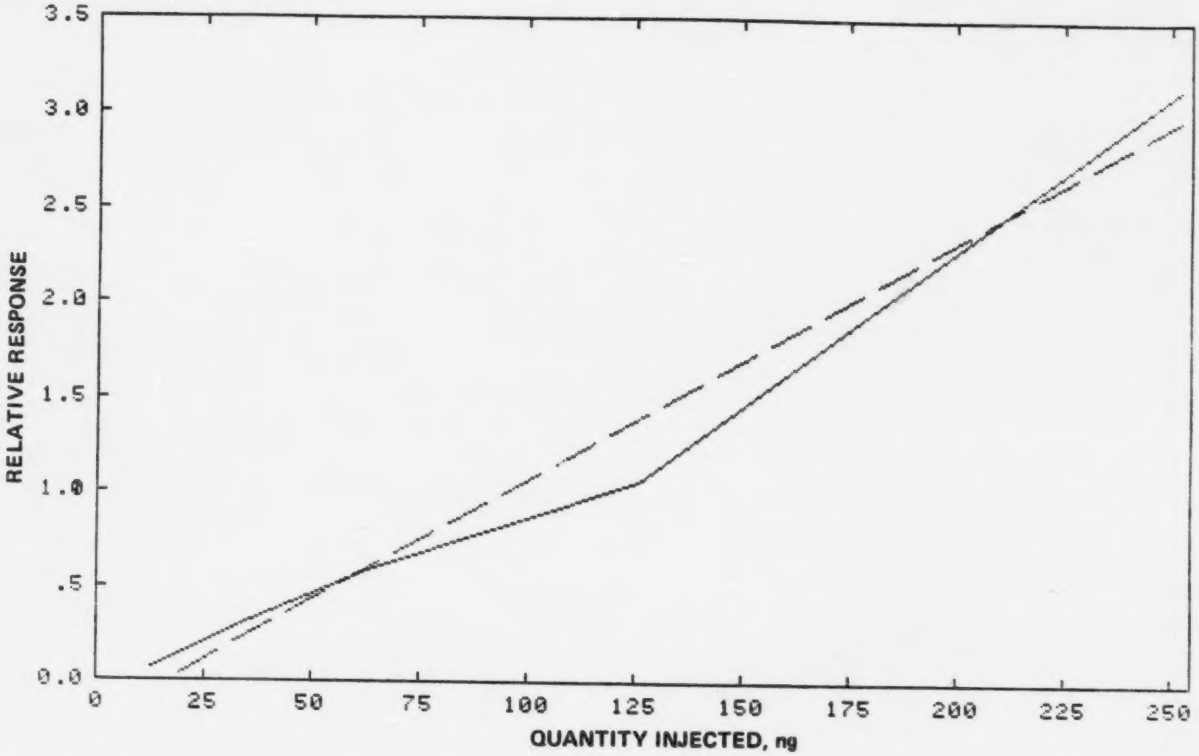
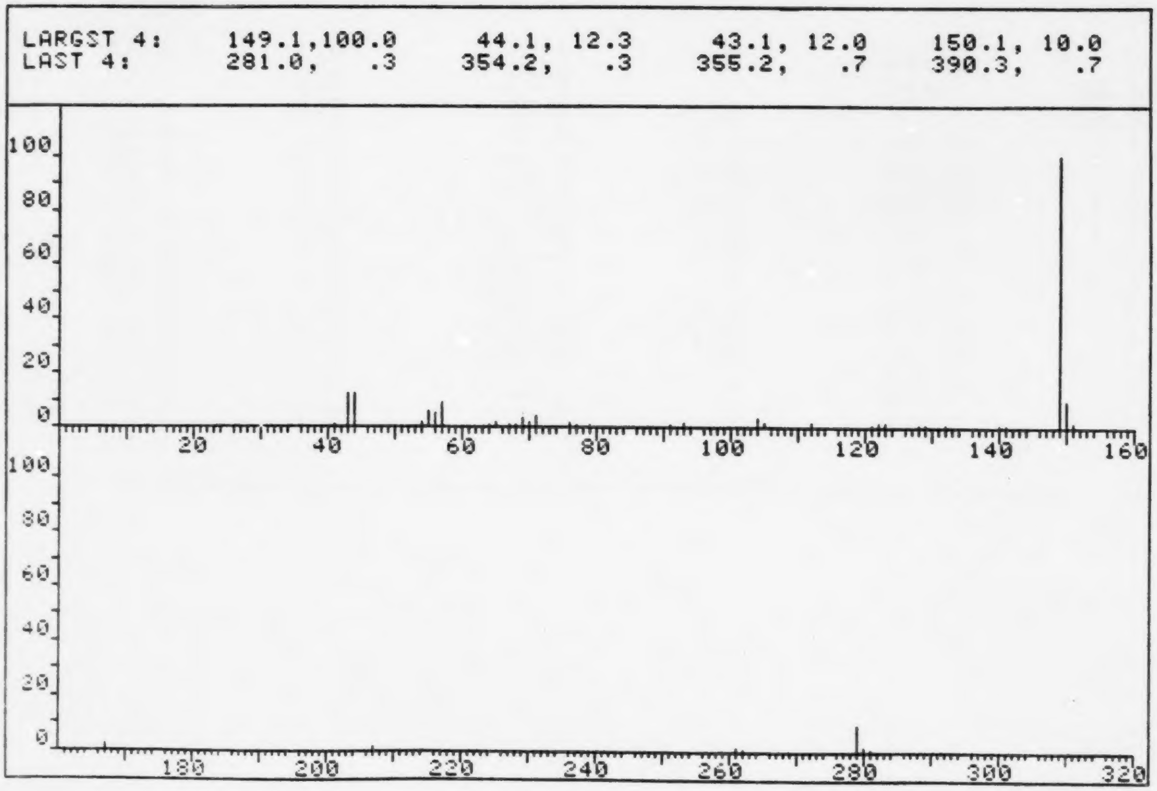


Figure B-62. Calibration curve for the determination of butylbenzyl phthalate by GC/MS.

Range: 63 - 250 ng
Correlation coefficient: 0.987
Slope: 1.3×10^{-2}
y-Intercept: -2.0×10^{-1}



```
LARGST 4:     149.1,100.0      44.1, 12.3      43.1, 12.0     150.1, 10.0
LAST 4:       281.0,    .3    354.2,    .3    355.2,    .7    390.3,    .7
```

Figure B-63. **Mass spectrum for dioctyl phthalate.**

TABLE B-28. KEY IONS AND RELATIVE ABUNDANCES FOR DIOCTYL PHTHALATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.1	1.0	77.1	1.0	141.0	.7
43.1	12.0	79.0	.7	149.1	100.0
44.1	12.3	91.1	.7	150.1	10.0
54.0	1.3	93.0	1.3	151.1	1.7
55.0	6.0	104.0	3.0	167.0	2.0
56.1	5.3	105.0	1.7	207.0	1.0
57.1	9.0	112.2	1.3	261.2	1.7
64.2	1.0	121.0	1.0	262.2	.3
65.2	1.3	122.1	1.7	279.2	9.3
67.0	.7	123.1	1.3	280.2	1.7
68.1	1.0	128.0	1.0	281.0	.3
69.1	3.7	129.2	.7	354.2	.3
70.0	1.7	132.2	.7	355.2	.7
71.0	4.3	140.2	.7	390.3	.7
76.0	1.7				

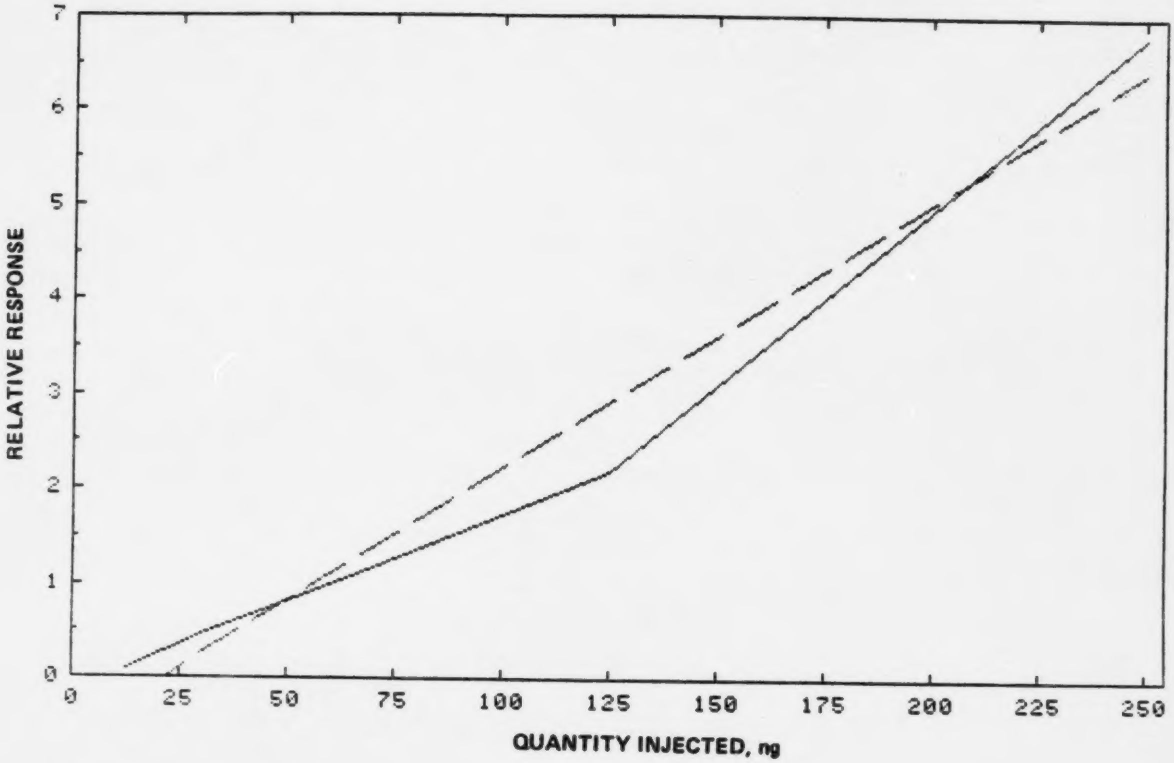


Figure B-64. Calibration curve for the determination of dioctyl phthalate by GC/MS.

Range: 50 - 250 ng
Correlation coefficient: 0.986
Slope: 2.8 x 10^{-2}
y-Intercept: -5.8 x 10^{-1}

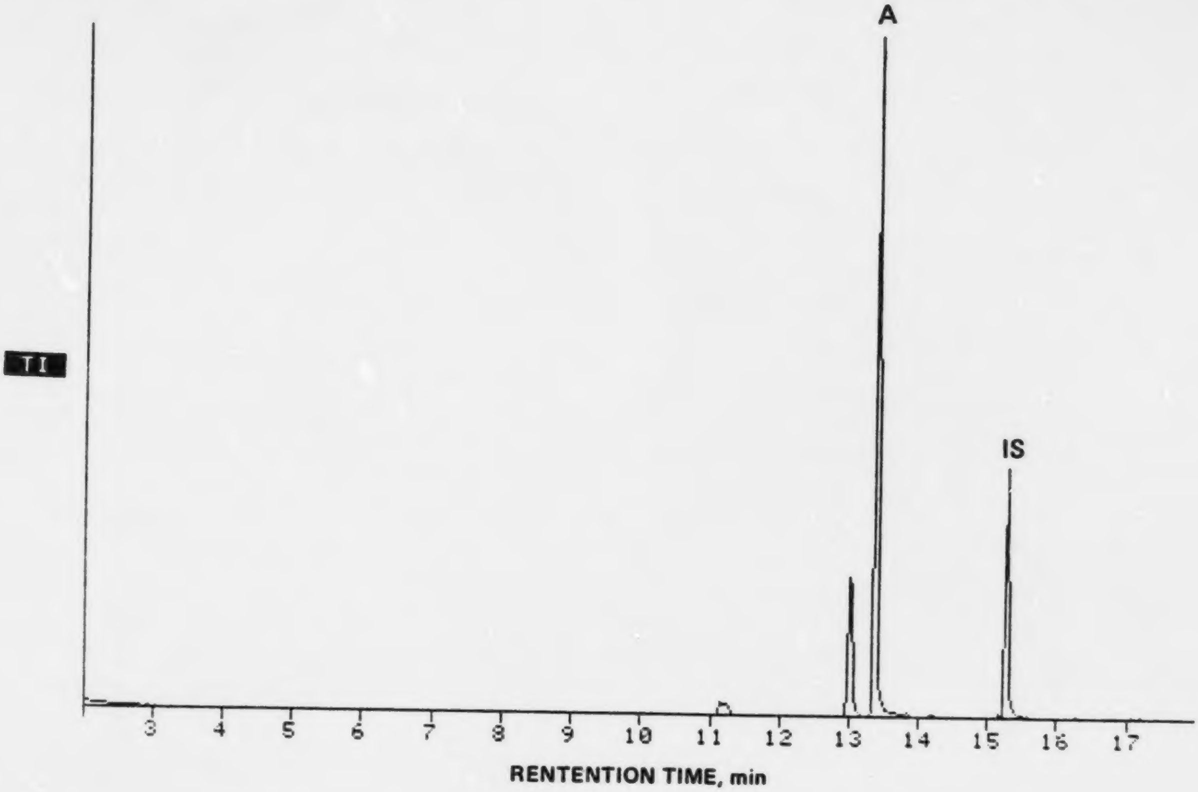
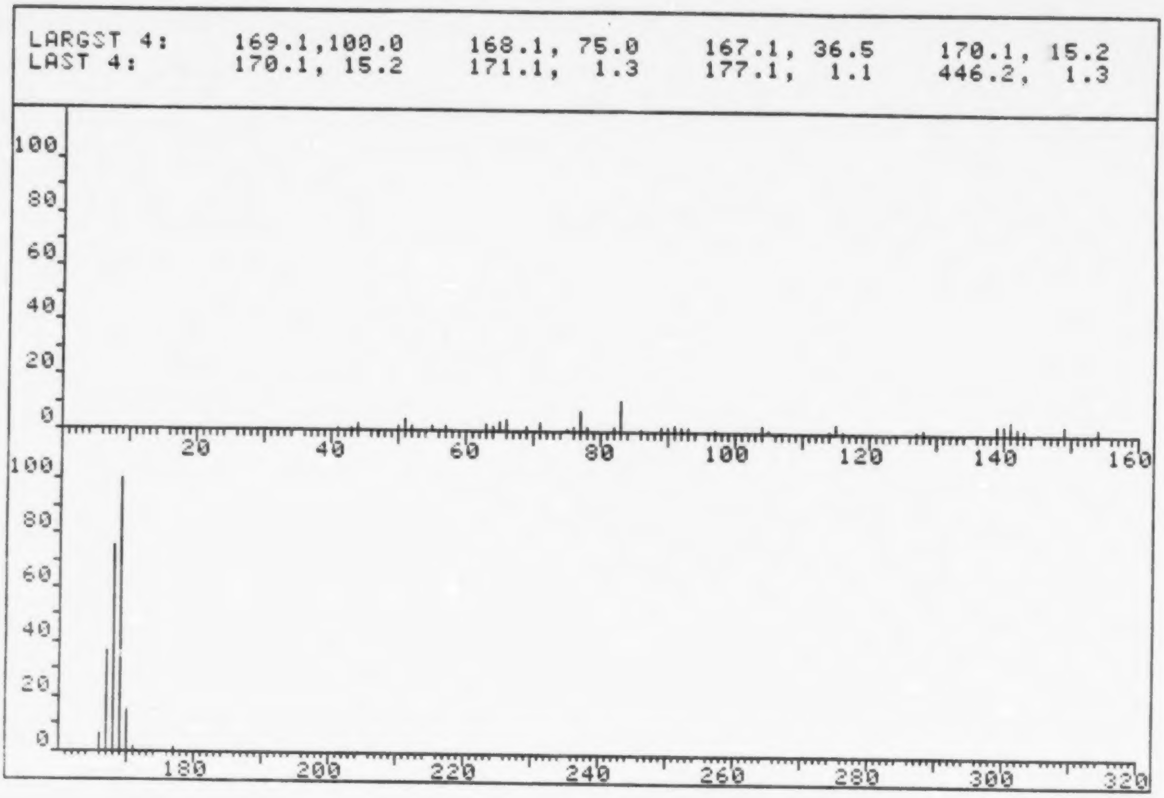


Figure B-65. Chromatogram by GC/MS for diphenylamine (t_R = 13.4 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:     169.1,100.0     168.1, 75.0     167.1, 36.5     170.1, 15.2
LAST 4:       170.1, 15.2     171.1,  1.3     177.1,  1.1     446.2,  1.3
```

Figure B-66. Mass spectrum for diphenylamine

TABLE B-29. KEY IONS AND RELATIVE ABUNDANCES FOR DIPHENYLAMINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.2	1.1	76.1	1.3	116.1	1.1
43.3	1.1	77.1	7.2	127.2	1.1
44.1	.7	78.1	1.5	128.1	2.0
50.1	1.5	82.6	2.0	139.1	3.7
51.1	4.6	83.6	11.5	140.1	3.5
52.1	1.5	89.1	1.5	141.2	4.8
55.1	1.3	90.1	1.3	142.1	2.4
57.1	1.3	91.1	2.4	143.2	1.5
63.1	2.2	92.1	1.3	154.1	2.4
64.0	1.7	93.1	1.5	166.1	6.3
65.1	2.6	97.2	1.1	167.1	36.5
66.1	4.6	104.1	2.2	168.1	75.0
69.3	1.3	105.1	1.1	169.1	100.0
70.8	1.5	114.0	1.1	170.1	15.2
74.9	1.1	115.1	3.3	171.1	1.3

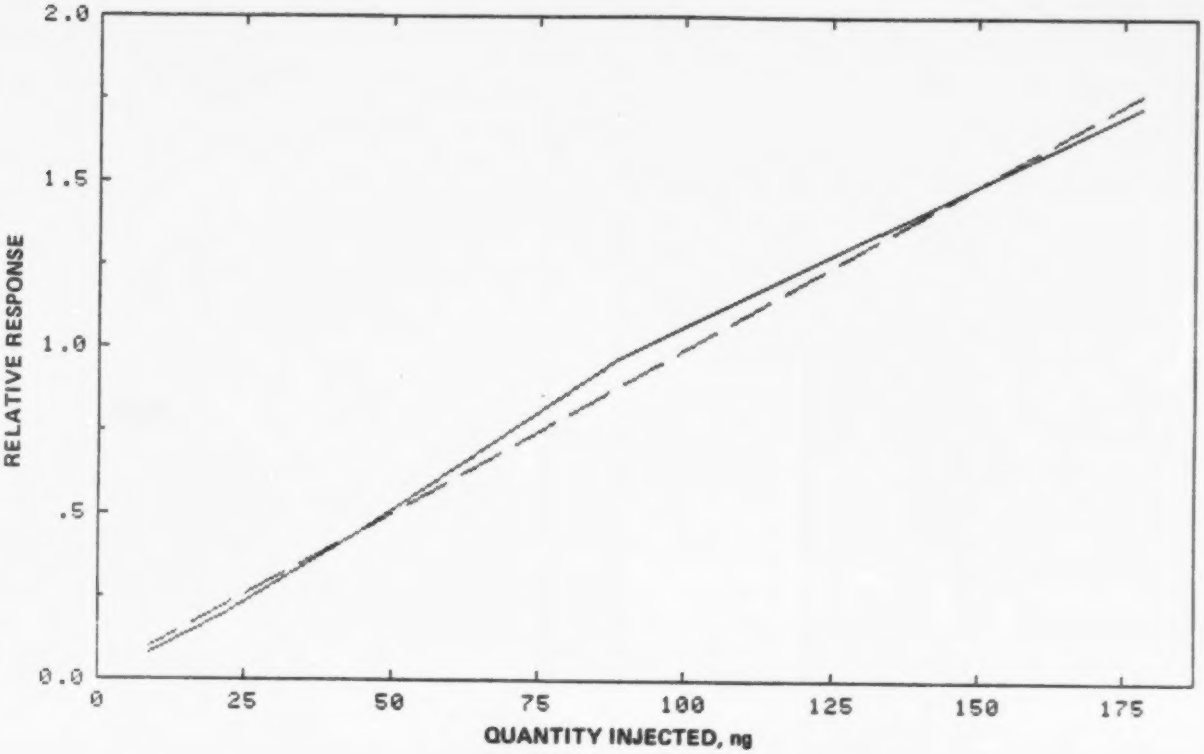


Figure B-67. Calibration curve for the determination of diphenylamine by GC/MS.

Range: 22 - 180 ng
Correlation coefficient: 0.998
Slope: 1.0×10^{-2}
y-Intercept: 1.0×10^{-2}

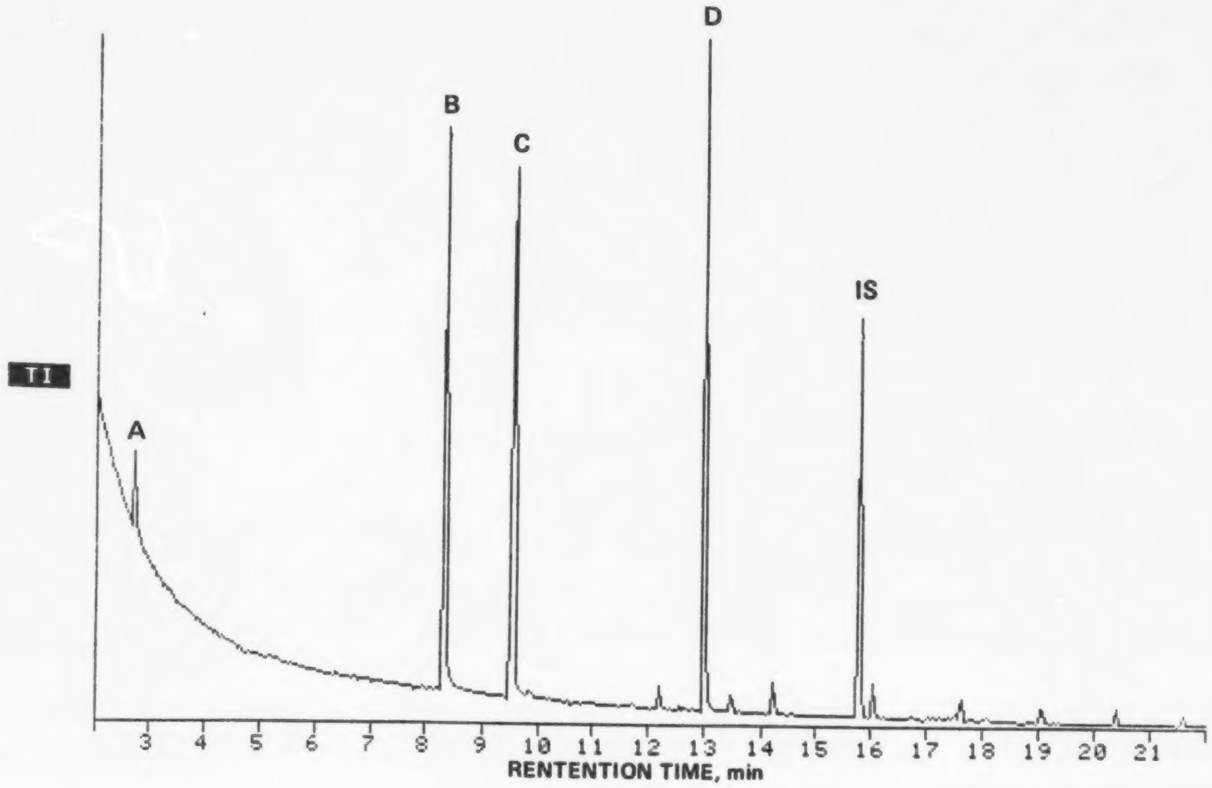


Figure B-68. Chromatogram by GC/MS for

(A) ethyl carbamate(t_R = 2.3 min),
(B) *o*-phenylenediamine(t_R = 7.8 min),
(C) *m*-phenylenediamine(t_R = 8.9 min), and
(D) 2-naphthylamine(t_R = 12.4 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

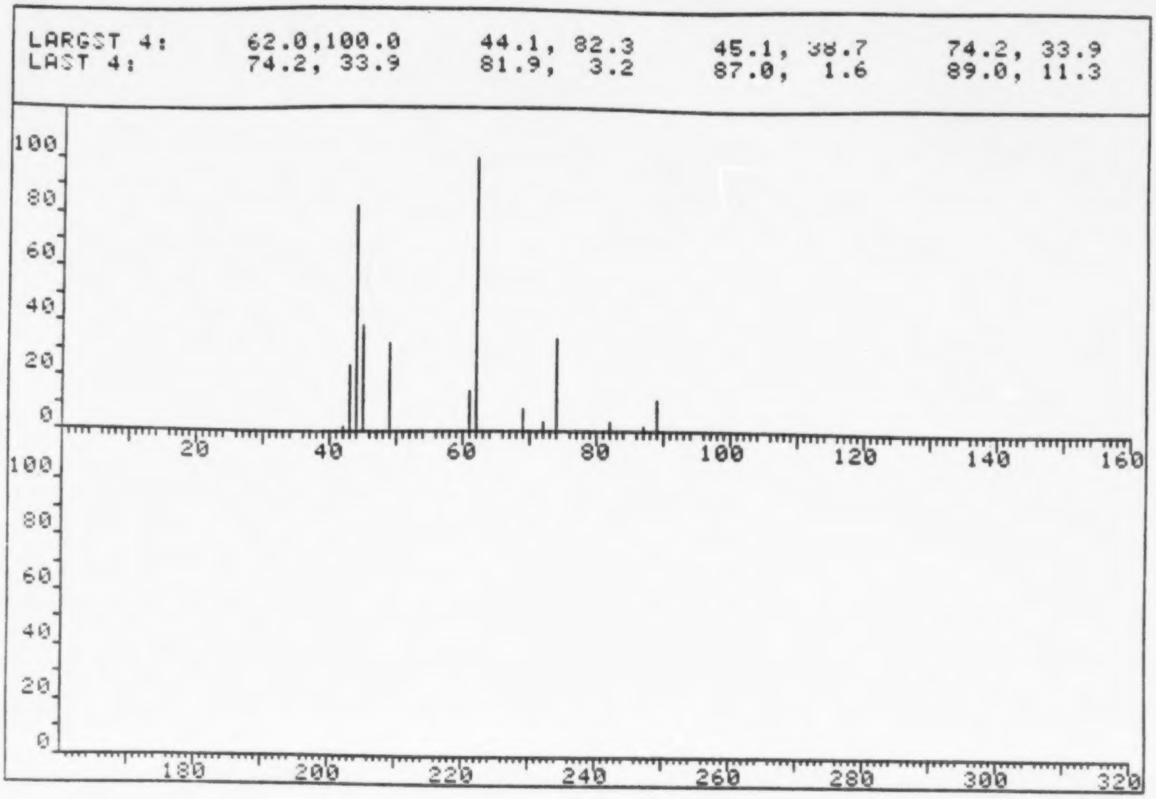


Figure B-69. Mass spectrum for ethyl carbamate.

TABLE B-30. KEY IONS AND RELATIVE ABUNDANCES FOR ETHYL CARBAMATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
42.1	19.4	45.1	38.7	69.0	1.6
43.1	24.2	61.1	14.5	74.2	33.9
44.1	91.9	62.0	100.0	89.0	11.3

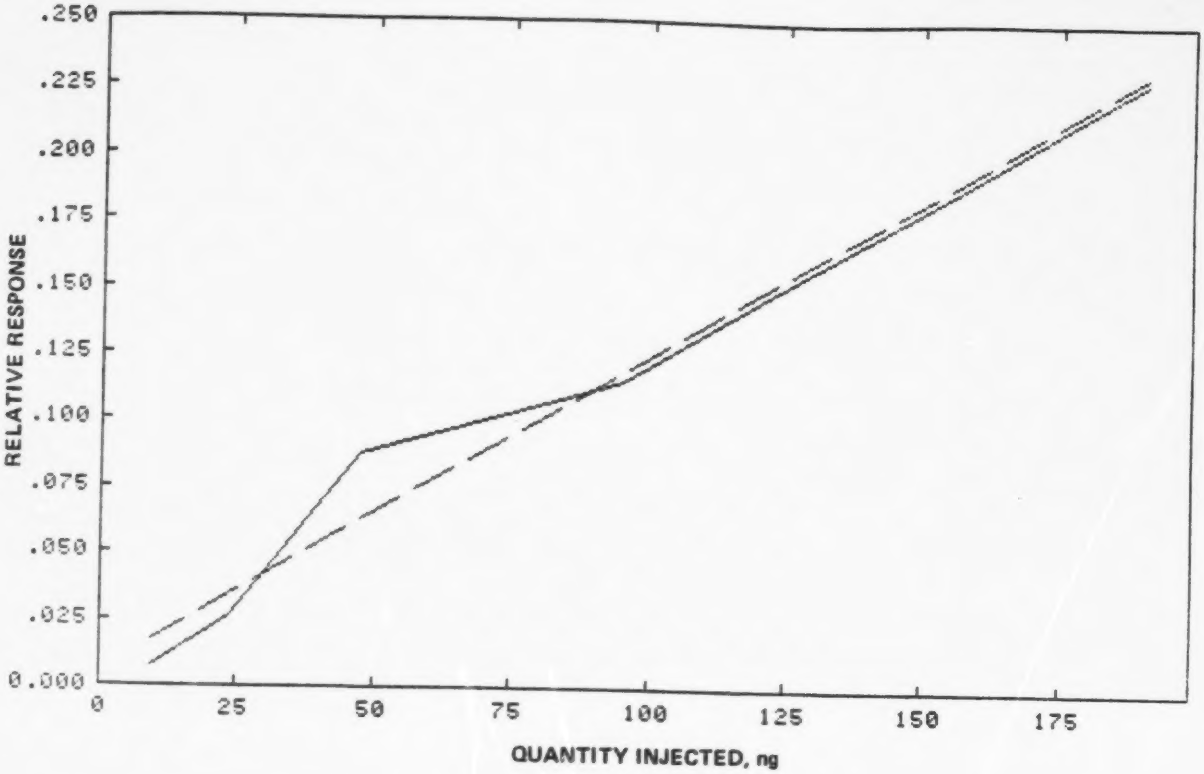
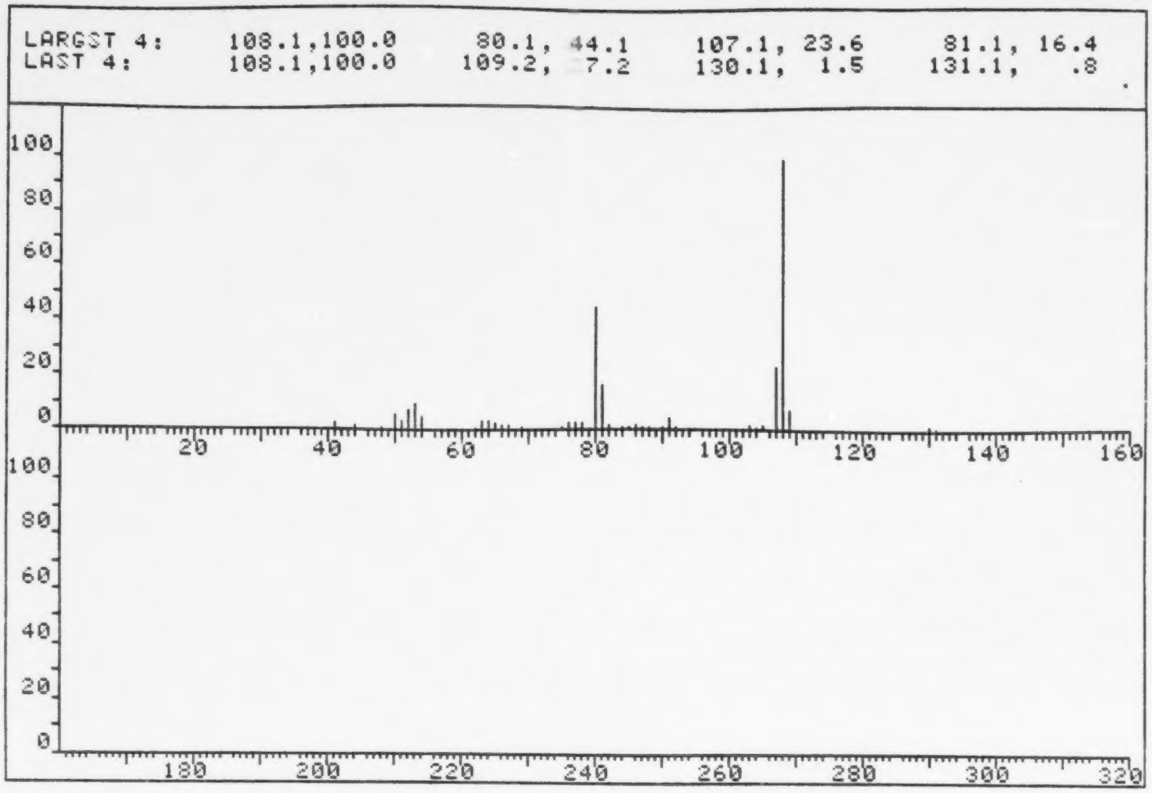


Figure B-70. Calibration curve for the determination of ethyl carbamate by GC/MS.

Range: 24 - 190 ng
Correlation coefficient: 0.987
Slope: 1.2×10^{-3}
y-Intercept: 6.4×10^{-3}



```
LARGST 4:     108.1,100.0      80.1, 44.1     107.1, 23.6      81.1, 16.4
LAST 4:       108.1,100.0     109.2,  7.2     130.1,  1.5     131.1,   .8
```

Figure B-71. Mass spectrum for o-phenylenediamine.

TABLE B-31. KEY IONS AND RELATIVE ABUNDANCES FOR o-PHENYLENEDIAMINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
44.0	2.5	69.0	.2	92.1	.8
52.1	5.4	75.1	1.2	103.1	1.5
53.1	9.5	76.0	2.5	104.2	1.2
54.1	4.8	77.1	1.9	105.1	1.4
62.1	1.2	78.0	2.5	107.1	23.6
63.1	3.5	80.1	44.1	108.1	100.0
64.0	3.3	81.1	16.4	109.2	7.2
65.0	2.3	90.0	1.2	130.1	1.5
66.1	1.4	91.1	4.3	131.1	.8
67.0	1.5				

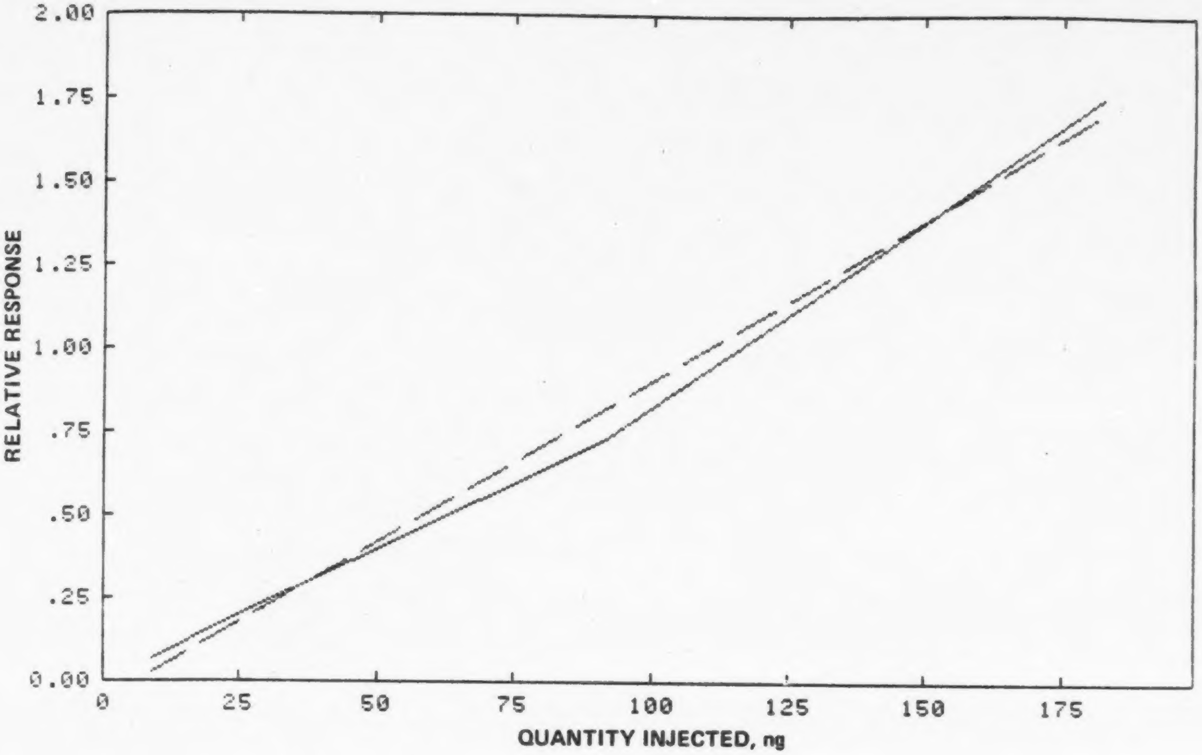
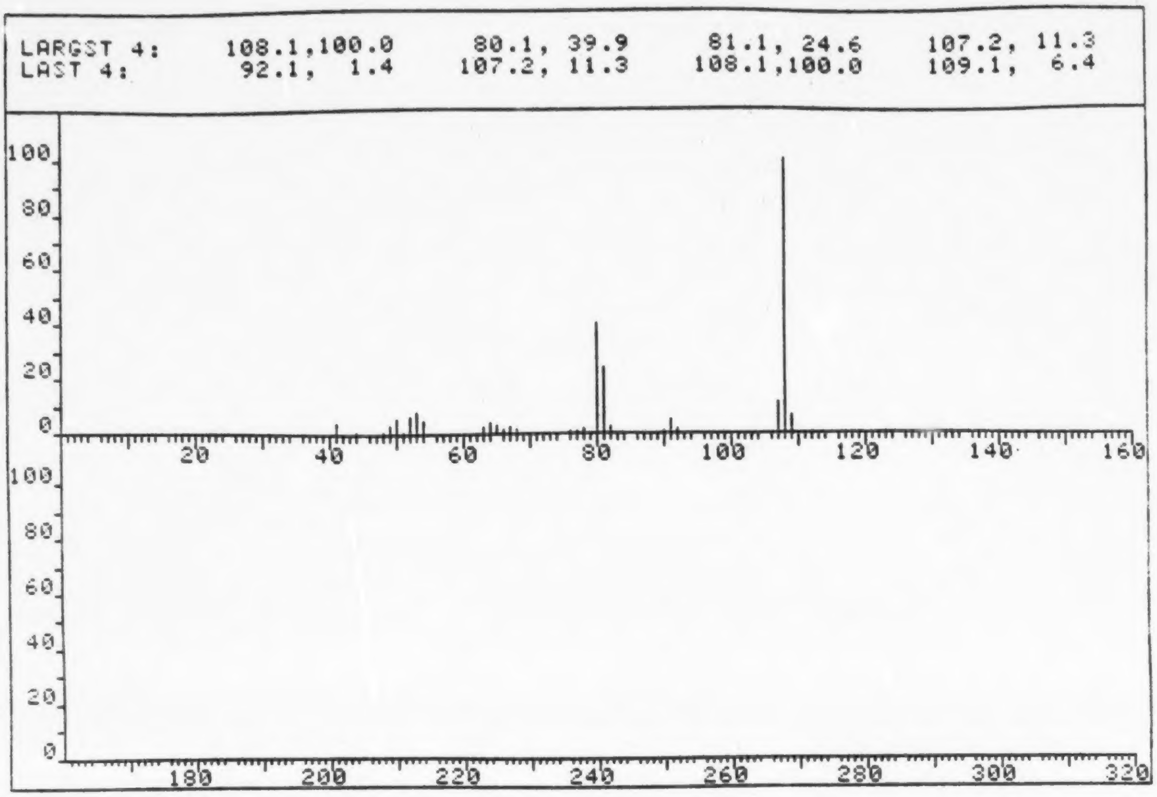


Figure B-72. Calibration curve for the determination of o-phenylenediamine by GC/MS.

Range: 23 - 180 ng
Correlation coefficient: 0.996
Slope: 9.7×10^{-3}
y-Intercept: -6.5×10^{-2}



```
LARGST 4:    108.1,100.0     80.1, 39.9     81.1, 24.6    107.2, 11.3
LAST 4:       92.1,  1.4    107.2, 11.3    108.1,100.0    109.1,  6.4
```

Figure B-73. Mass spectrum for m-phenylenediamine.

TABLE B-32. KEY IONS AND RELATIVE ABUNDANCES FOR *m*-PHENYLENEDIAMINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.1	1.8	65.1	2.5	81.1	22.5
42.1	1.0	66.0	1.5	82.1	1.2
43.1	.3	67.0	1.8	89.0	.1
44.1	.4	68.1	.7	90.0	1.1
52.1	4.7	69.1	.4	91.1	5.2
53.1	6.2	73.1	.1	92.1	.7
54.1	3.3	74.0	.2	93.1	.5
55.0	.7	75.0	.3	105.1	.7
56.0	.3	76.1	.6	107.1	11.0
61.0	.5	77.0	.3	108.1	100.0
62.0	.9	78.0	1.2	109.1	6.7
63.1	2.3	80.0	37.6	110.2	.2
64.0	2.5				

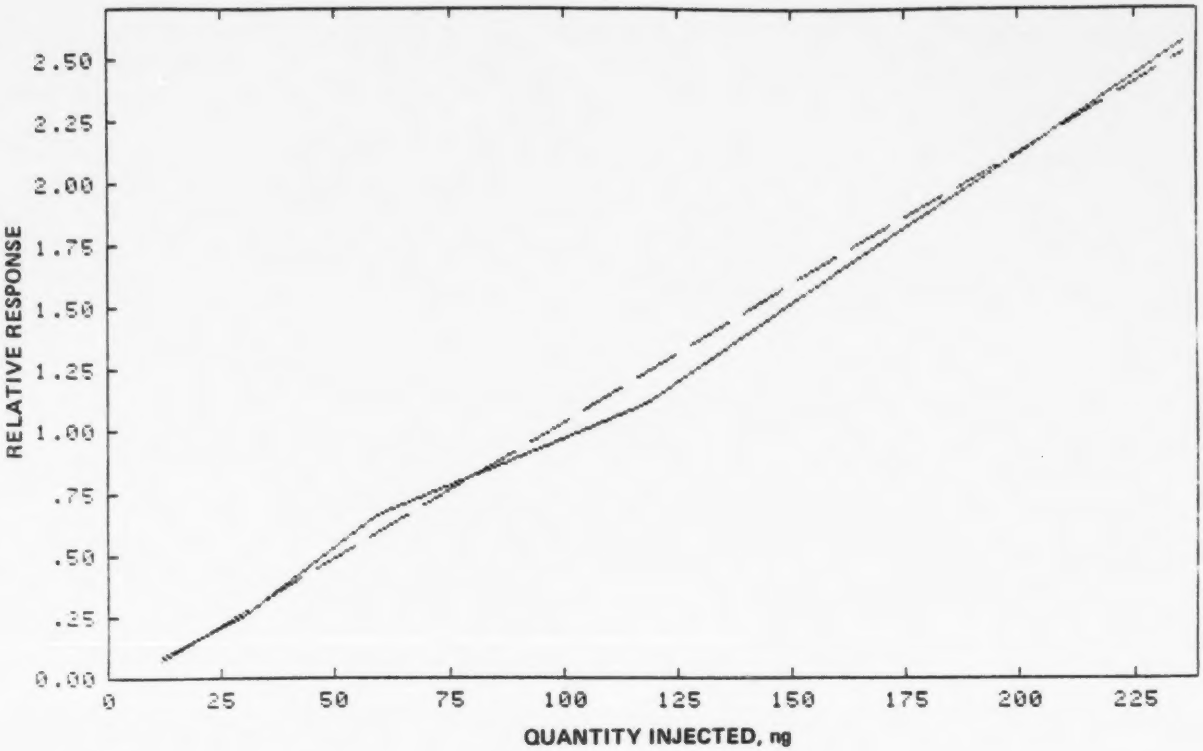
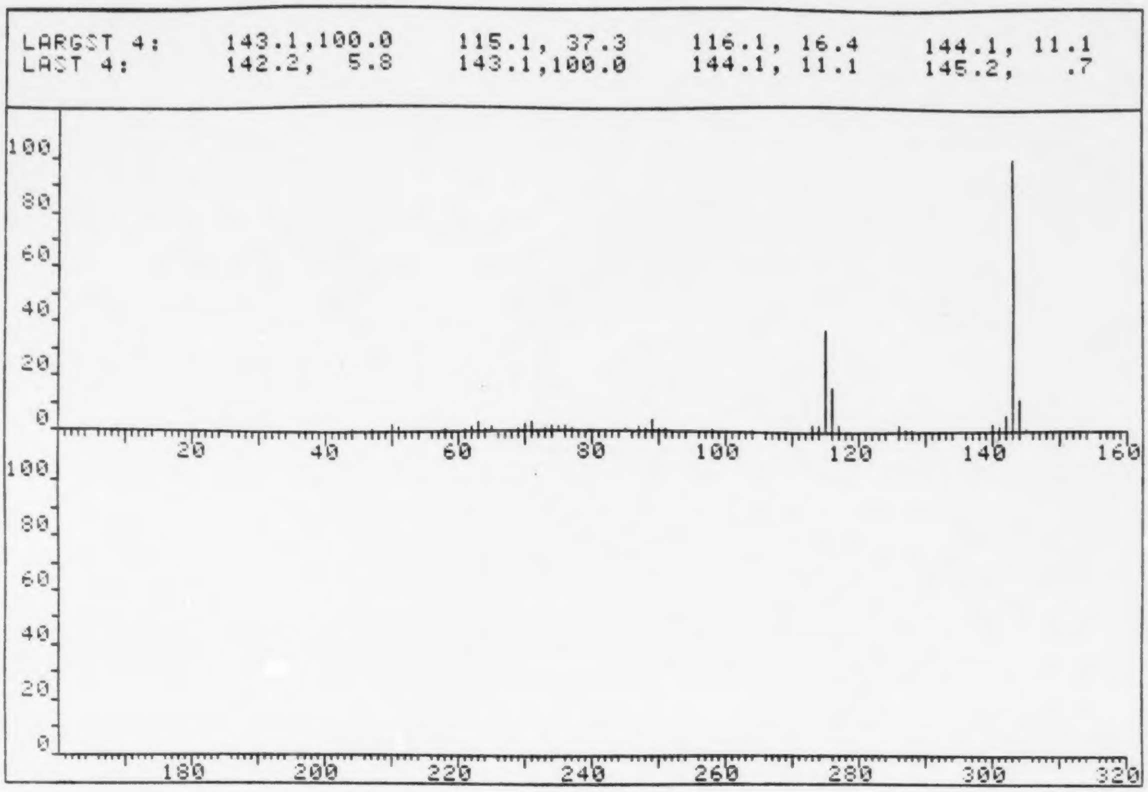


Figure B-74. Calibration curve for the determination of m-phenylenediamine by GC/MS.

Range: 12 - 240 ng
Correlation coefficient: 0.997
Slope: 1.1×10^{-2}
y-Intercept: -6.1×10^{-2}



```
LARGST 4:     143.1,100.0     115.1, 37.3     116.1, 16.4     144.1, 11.1
LAST 4:       142.2,   5.8    143.1,100.0     144.1, 11.1     145.2,    .7
```

Figure B-75. Mass spectrum for 2-naphthylamine.

TABLE B-33. KEY IONS AND RELATIVE ABUNDANCES FOR 2-NAPHTHYLAMINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
44.1	1.9	76.0	1.5	116.1	16.4
58.6	1.0	77.1	.5	117.1	2.4
61.2	.9	89.1	4.1	126.1	2.1
62.1	1.5	90.2	1.0	127.1	.7
63.1	3.3	91.1	.9	128.1	1.0
64.0	.9	98.2	.7	140.0	2.2
65.0	1.4	104.0	.9	141.1	1.4
70.5	2.7	108.2	.7	142.2	5.8
71.6	1.9	113.1	2.4	143.1	100.0
73.0	.7	114.1	2.7	144.1	11.1
74.0	1.5	115.1	37.3	145.2	.7
75.1	1.4				

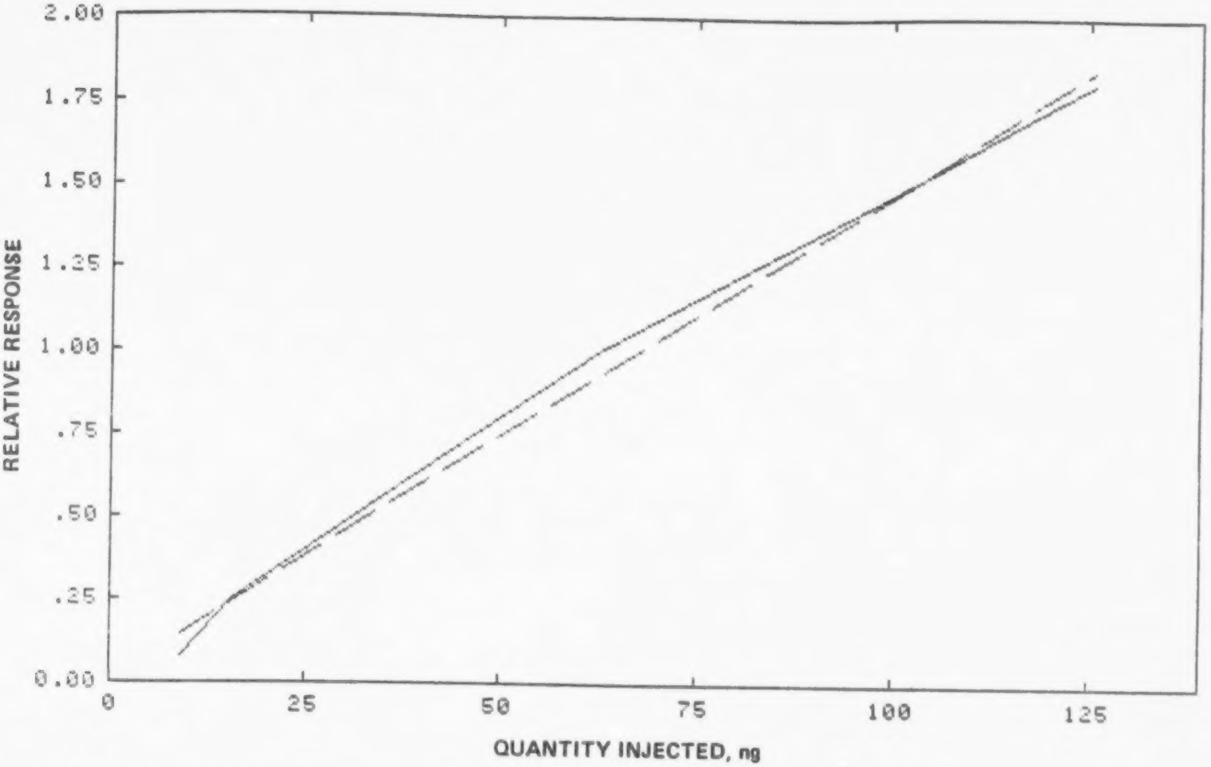


Figure B-76. Calibration curve for the determination of 2-naphthylamine by GC/MS.

Range: 16 - 130 ng
Correlation coefficient: 0.997
Slope: 1.5×10^{-2}
y-Intercept: 1.3×10^{-2}

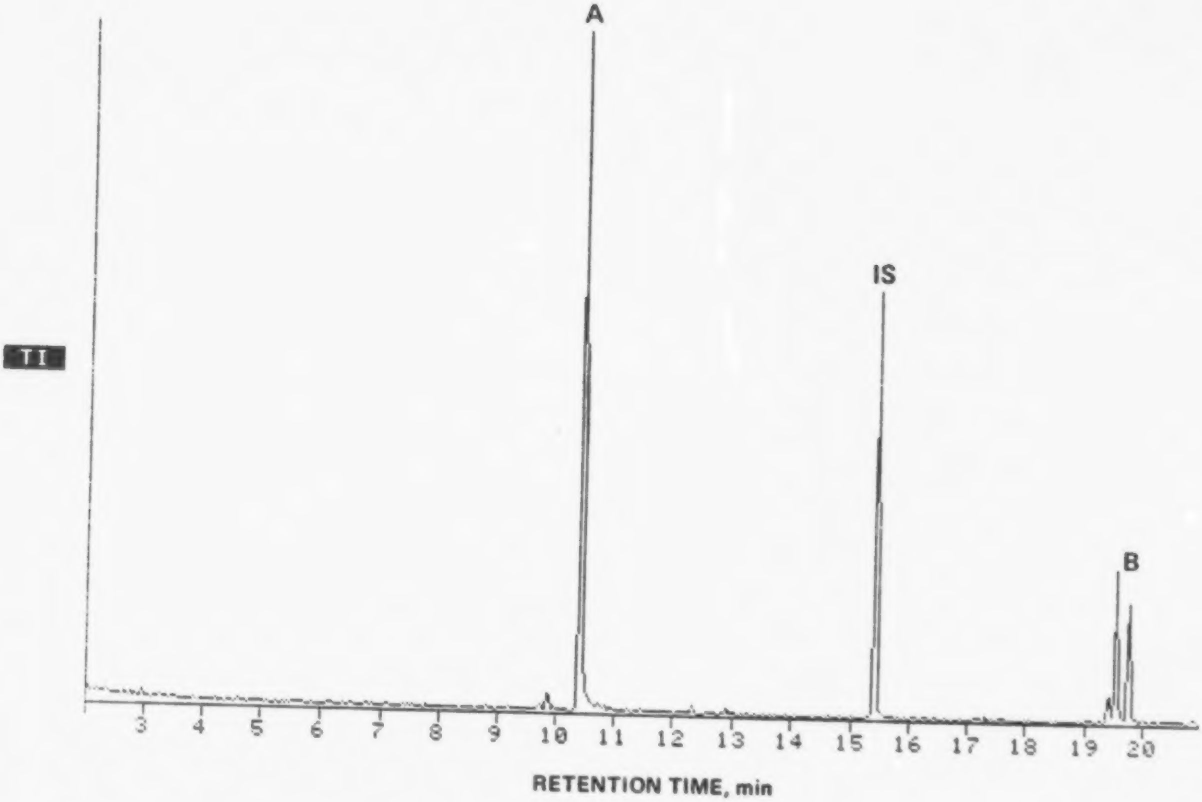


Figure B-77. Chromatogram by GC/MS for

(A) isosafrole(t_R = 10.3 min) and
(B) aramite(t_R = 19.5 and 19.8 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

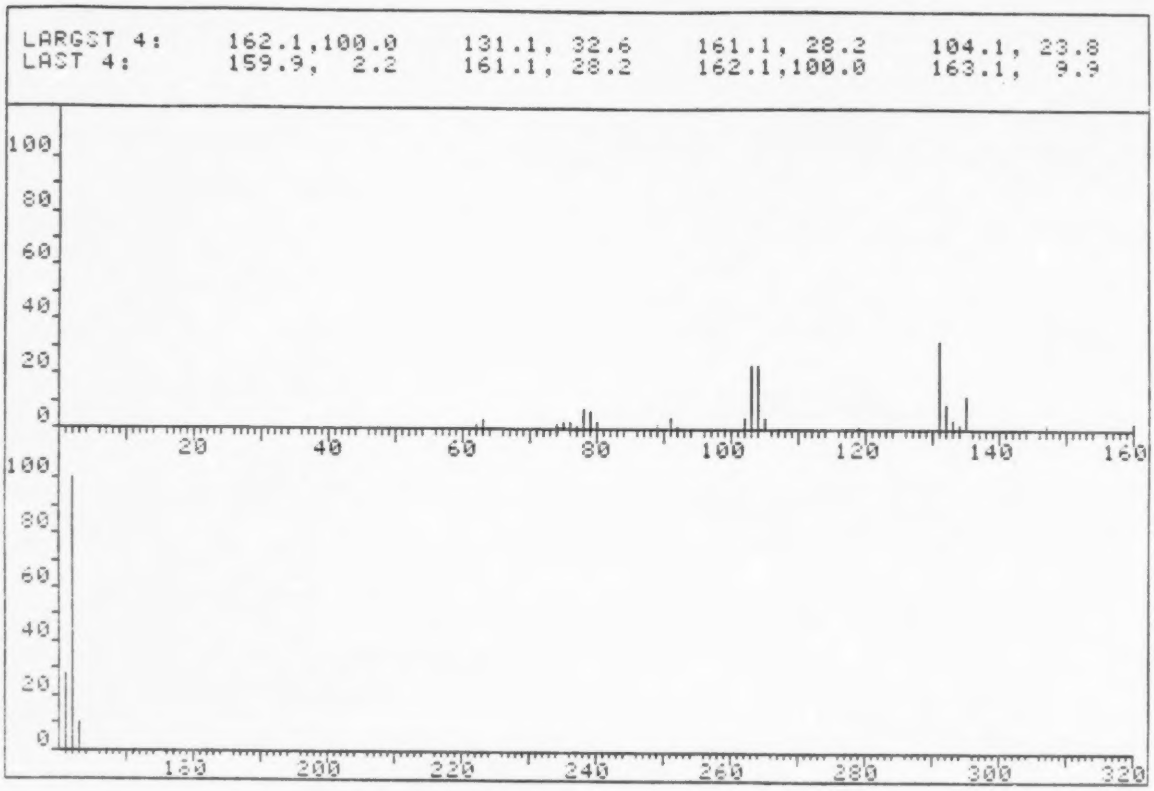


Figure B-78. Mass spectrum for isosafrole.

TABLE B-34. KEY IONS AND RELATIVE ABUNDANCES FOR ISOSAFROLE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
45.0	.2	78.1	13.3	116.1	.3
45.7	.3	79.1	5.4	117.1	.4
50.0	1.5	80.1	2.8	118.0	.3
51.1	3.1	81.0	4.1	119.1	1.6
52.1	1.8	87.0	.5	120.0	.5
53.2	1.4	89.1	2.7	121.1	.9
55.0	.4	90.1	.7	122.1	.6
59.7	.2	91.1	6.4	129.1	.2
60.0	.2	92.1	1.2	131.1	37.4
61.1	.8	93.0	.2	132.1	10.8
62.0	2.8	95.0	.2	133.2	2.2
63.0	5.7	98.1	.5	134.1	1.3
64.0	1.0	100.2	.2	135.1	14.2
65.1	2.9	101.1	.9	136.1	1.5
66.0	1.1	102.1	5.2	145.1	.5
67.1	.2	103.1	26.5	146.1	.4
67.9	.0	104.1	31.7	147.1	.9
72.3	.1	105.1	6.6	148.2	.2
73.1	.8	106.1	1.0	159.1	.3
74.1	2.5	107.1	.5	161.1	29.1
75.1	2.7	108.0	.3	162.1	100.0
76.1	4.0	114.0	.2	163.1	10.0
77.1	17.0	115.2	1.5	164.1	.9

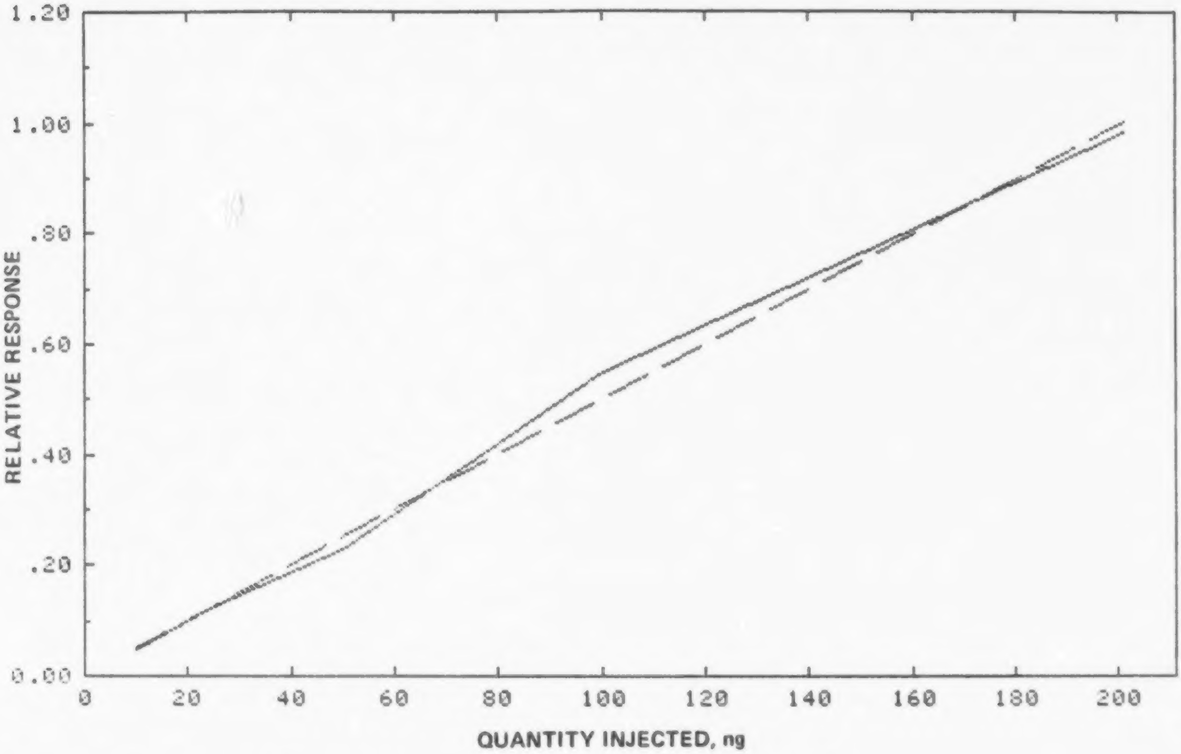


Figure B-79. Calibration curve for the determination of isosafrole by GC/MS.

Range: 25 - 200 ng
Correlation coefficient: 0.997
Slope: 5.0×10^{-3}
y-Intercept: 3.1×10^{-3}

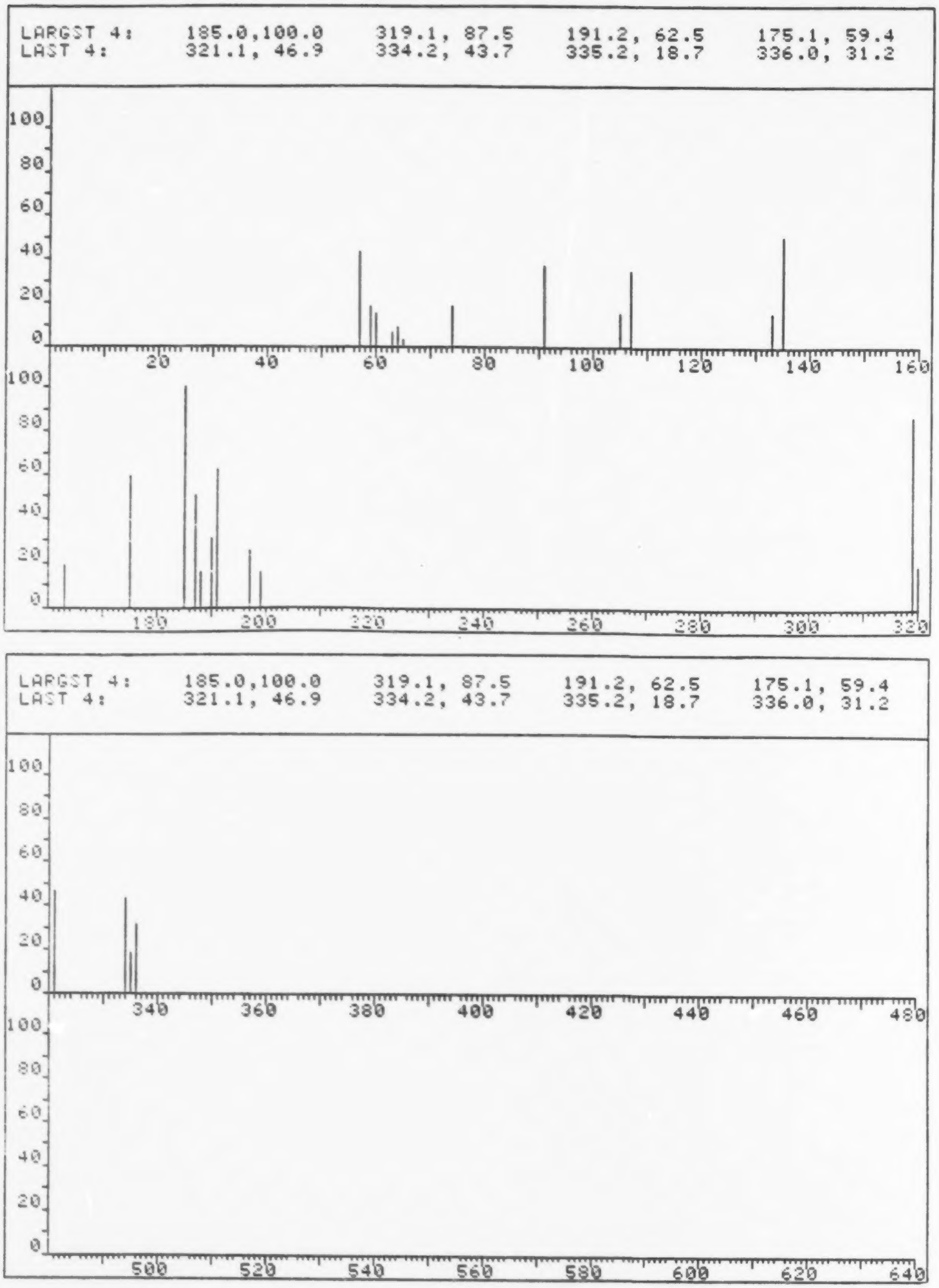


Figure B-80. Mass spectrum for aramite.

TABLE B-35. KEY IONS AND RELATIVE ABUNDANCES FOR ARAMITE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
57.2	43.7	107.1	34.4	191.2	62.5
59.2	18.7	133.1	15.6	197.2	25.0
59.9	15.6	135.2	50.0	199.0	15.6
63.0	6.2	163.3	18.7	319.1	87.5
64.0	9.4	175.1	59.4	320.2	18.7
65.0	3.1	185.0	100.0	321.1	46.9
74.2	18.7	187.0	50.0	334.2	43.7
91.1	37.5	188.2	15.6	335.2	18.7
105.0	15.6	190.2	31.2	336.0	31.2

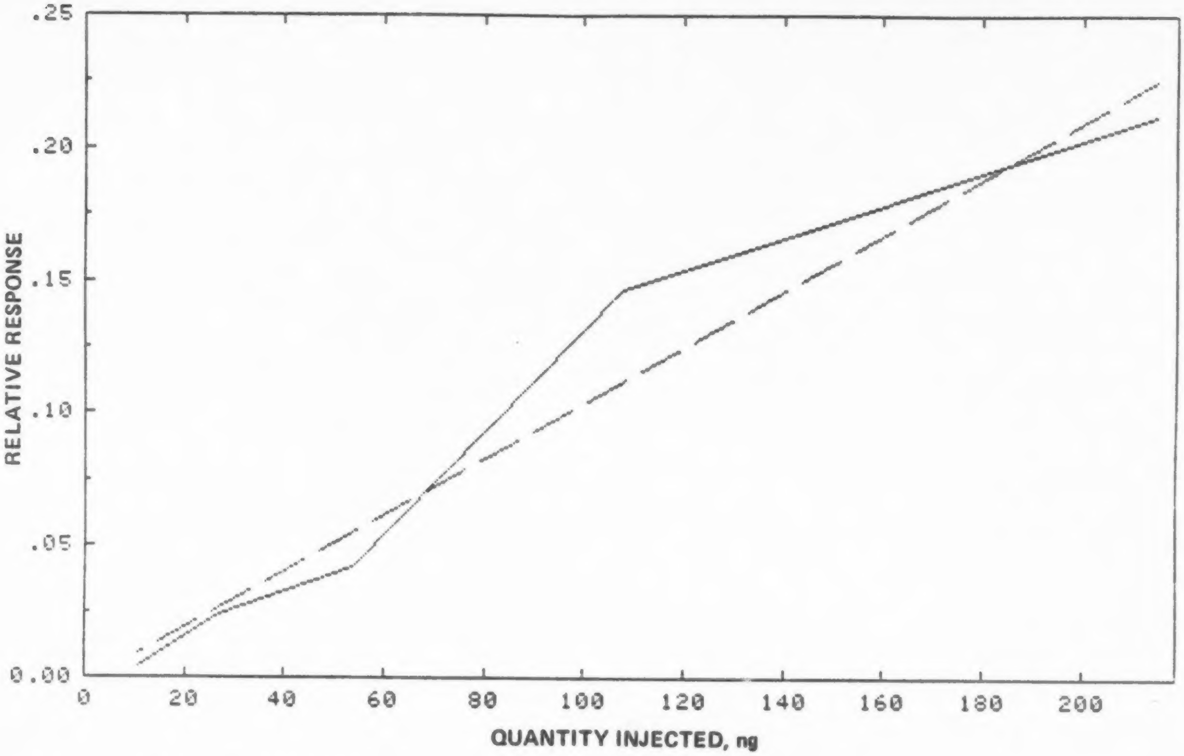


Figure B-81. Calibration curve for the determination of aramite by GC/MS.

Range: 27 - 220 ng
Correlation coefficient: 0.976
Slope: 1.1×10^{-3}
y-Intercept: -2.1×10^{-3}

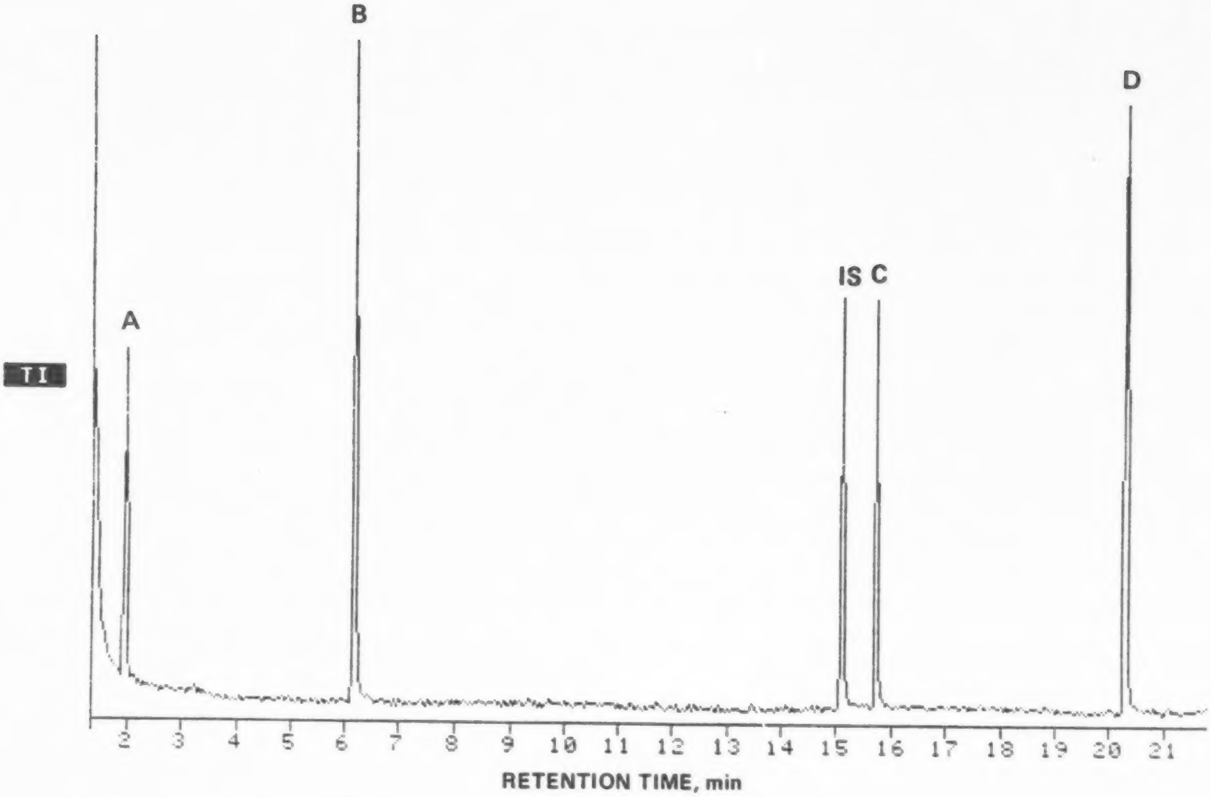
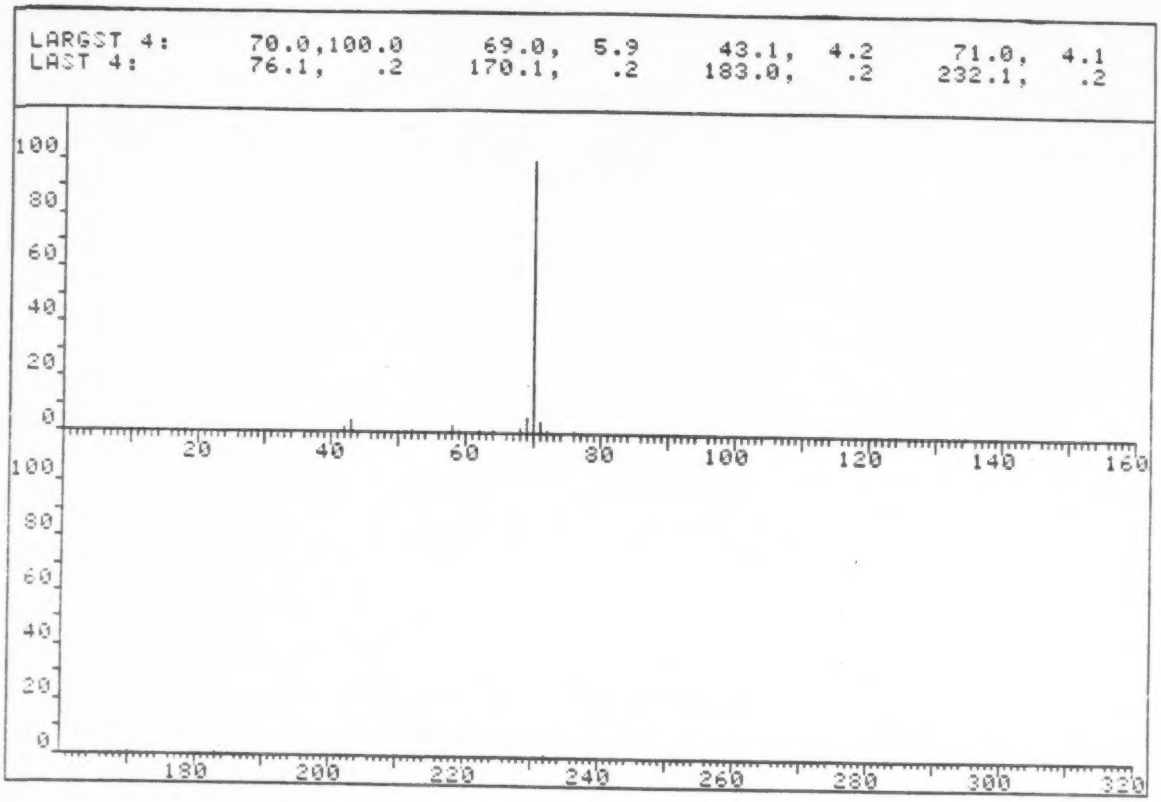


Figure B-82. Chromatogram by GC/MS for

(A) 2-methyllactonitrile(t_R = 1.7 min),
(B) p-cresol(t_R = 5.8 min),
(C) dimethoate(t_R = 14.7 min), and
(D) chlorobenzilate(t_R = 20.0 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:     70.0,100.0     69.0,  5.9     43.1,  4.2     71.0,  4.1
LAST 4:       76.1,    .2   170.1,   .2    183.0,   .2    232.1,   .2
```

Figure B-83. **Mass spectrum for 2-methyllactonitrile.**

TABLE B-36. KEY IONS AND RELATIVE ABUNDANCES FOR 2-METHYLLACTONITRILE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
42.1	2.0	63.9	.1	71.9	.1
43.1	4.2	68.0	1.4	76.1	.2
52.0	.5	69.0	5.9	170.1	.2
58.0	2.2	70.0	100.0	183.0	.2
59.0	.8	71.0	4.1	232.1	.2
61.9	.1				

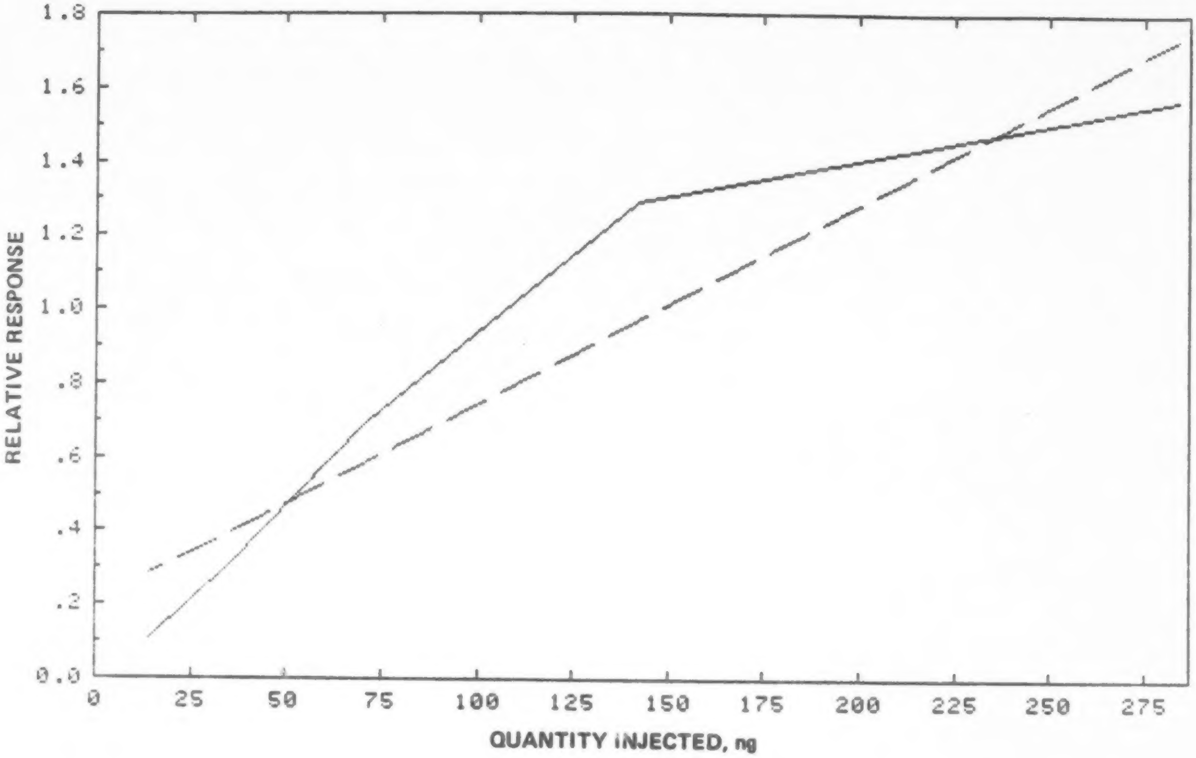
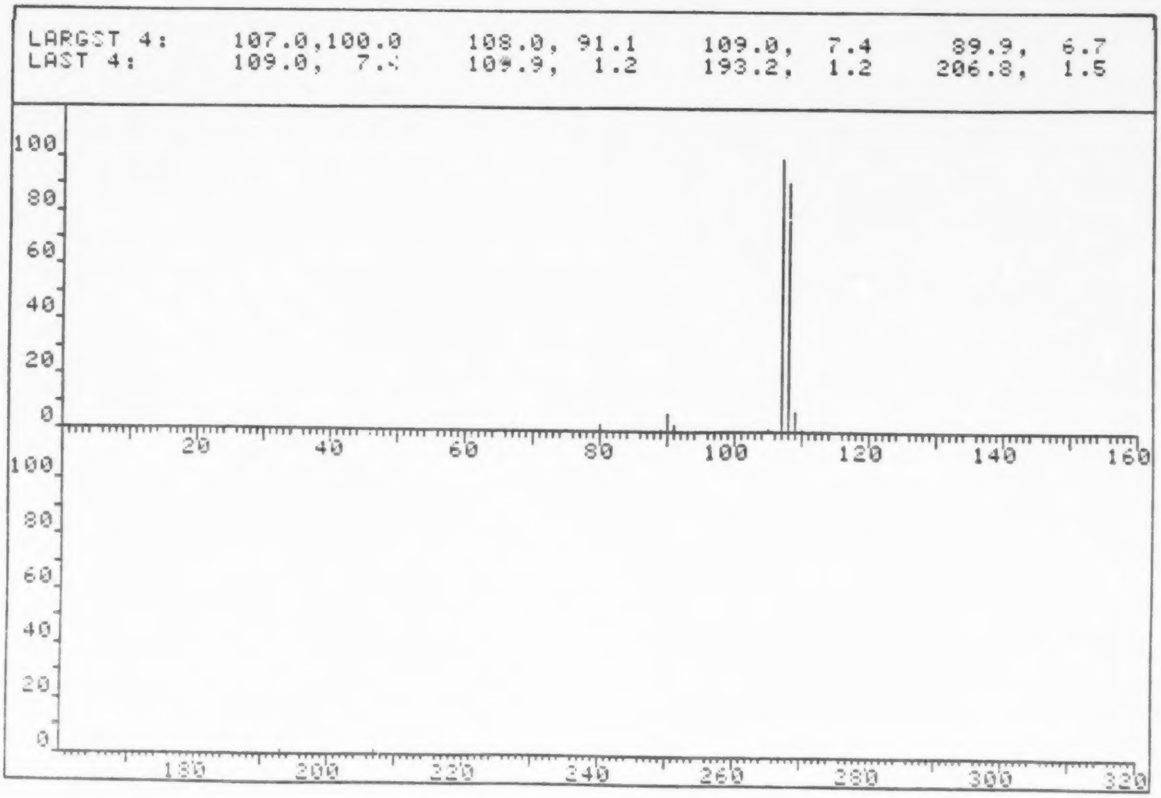


Figure B-84. Calibration curve for the determination of 2-methyllactonitrile by GC/MS.

Range: 36 - 280 ng
Correlation coefficient: 0.941
Slope: 5.4×10^{-3}
y-Intercept: 2.0×10^{-1}



```
LARGST 4:     107.0,100.0     108.0, 91.1     109.0,  7.4      89.9,  6.7
LAST 4:       109.0,  7.4     109.9,  1.2     193.2,  1.2     206.8,  1.5
```

Figure B-85. Mass spectrum for p-cresol.

TABLE B-37. KEY IONS AND RELATIVE ABUNDANCES FOR *p*-CRESOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
80.0	2.7	105.0	1.2	109.9	1.2
89.0	1.2	107.0	100.0	193.2	1.2
89.9	6.7	108.0	91.1	206.3	1.5
90.9	2.7	109.0	7.4		

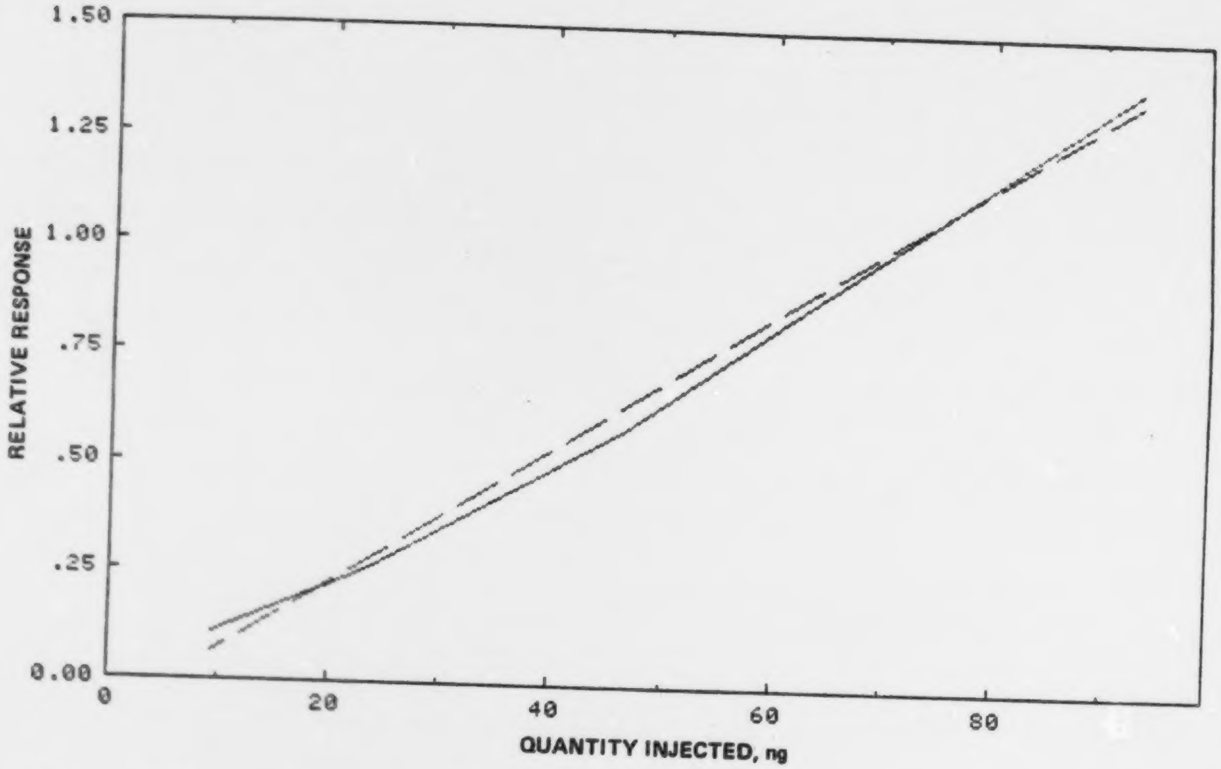
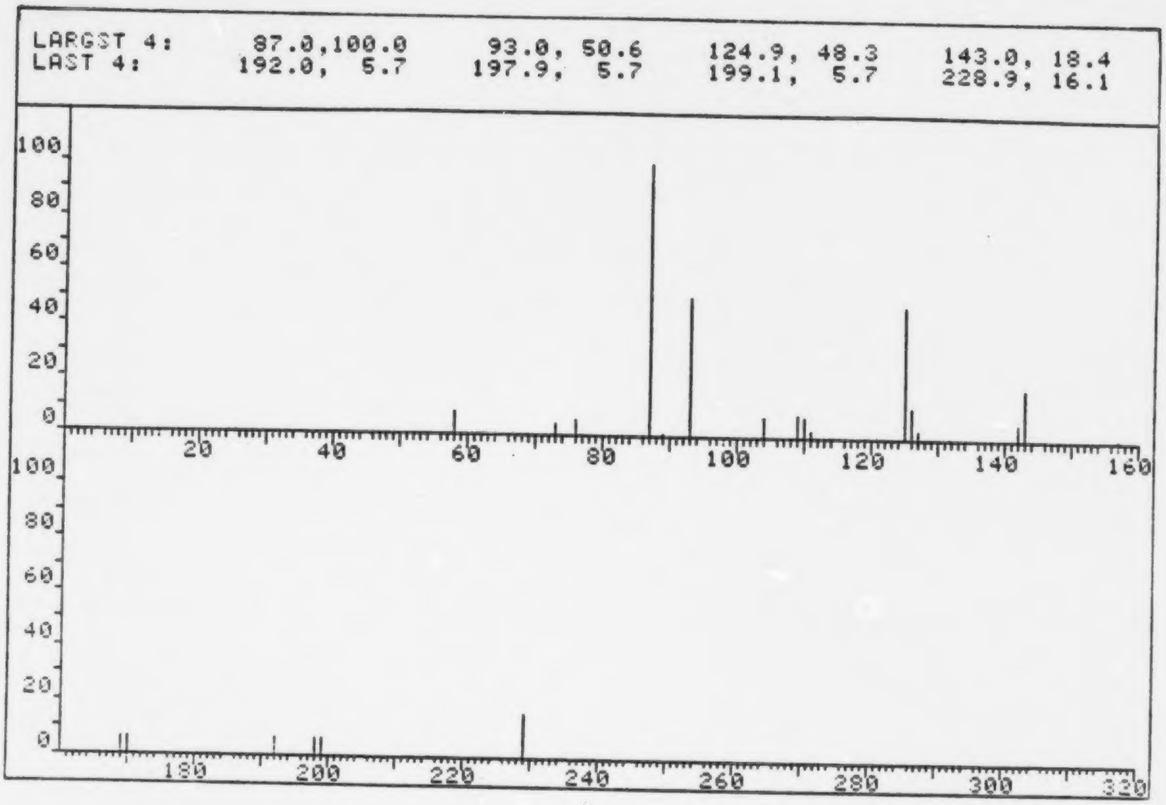


Figure B-86. Calibration curve for the determination of *p*-cresol by GC/MS.

Range: 23 - 100 ng
Correlation coefficient: 0.997
Slope: 1.5 x 10^{-2}
y-Intercept: -8.2 x 10^{-2}



```
LARGST 4:     87.0,100.0      93.0, 50.6     124.9, 48.3     143.0, 18.4
LAST 4:      192.0,   5.7    197.9,   5.7    199.1,   5.7    228.9, 16.1
```

Figure B-87.   Mass spectrum for dimethoate.

TABLE B-38. KEY IONS AND RELATIVE ABUNDANCES FOR DIMETHOATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
58.1	8.0	109.9	6.9	156.9	1.1
73.2	4.6	110.8	2.3	168.8	5.7
75.9	5.7	124.9	48.3	169.9	5.7
87.0	100.0	126.1	11.5	192.0	5.7
88.7	1.1	127.1	3.4	197.9	5.7
93.0	50.6	141.8	5.7	199.1	5.7
103.9	6.9	143.0	18.4	228.9	16.1
109.0	8.0				

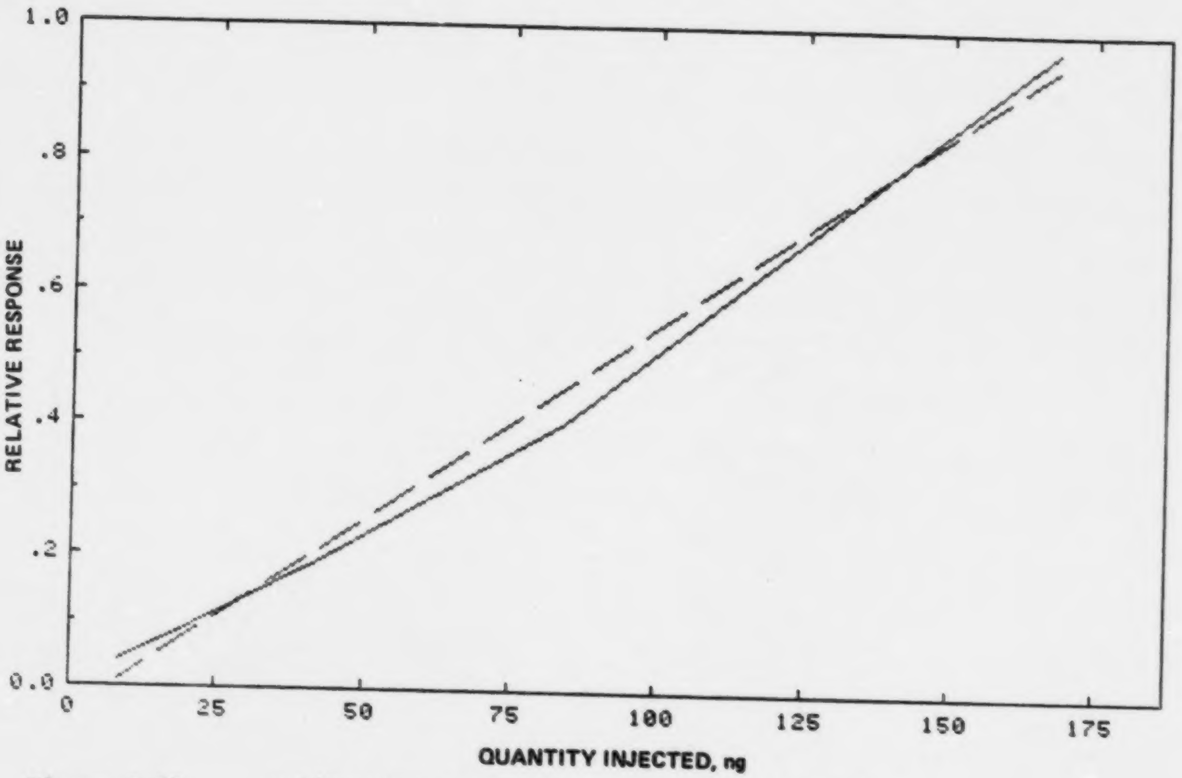
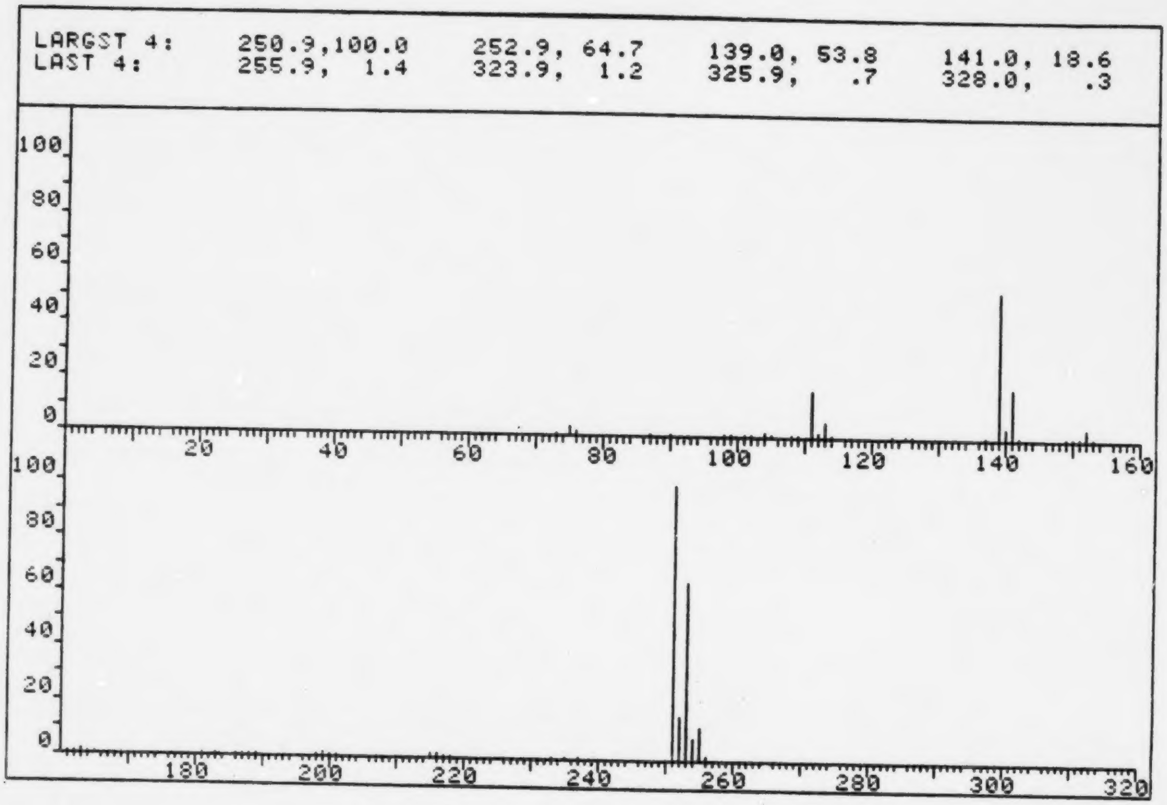


Figure B-88. Calibration curve for the determination of dimethoate by GC/MS.

Range: 21 - 170 ng
Correlation coefficient: 0.996
Slope: 5.9×10^{-3}
y-Intercept: -3.9×10^{-2}



```
LARGST 4:    250.9,100.0    252.9, 64.7    139.0, 53.8    141.0, 18.6
LAST 4:      255.9,   1.4   323.9,  1.2    325.9,    .7   328.0,    .3
```

Figure B-89. Mass spectrum for chlorobenzilate.

TABLE B-39. KEY IONS AND RELATIVE ABUNDANCES FOR CHLOROBENZILATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
72.8	.4	137.1	.4	189.1	.3
75.0	3.0	139.0	53.8	198.0	.3
76.0	1.7	140.0	4.0	199.0	1.6
87.1	.1	141.0	18.6	200.0	.3
89.9	.7	142.0	1.0	201.0	.5
98.2	.3	148.9	.4	215.0	1.3
98.9	.5	150.0	.8	216.0	1.3
99.4	.4	151.0	1.3	217.0	.6
101.0	.5	152.0	4.2	218.0	.5
101.9	.3	153.0	.7	233.0	.1
104.0	1.7	161.0	.4	235.0	.8
105.0	1.1	162.0	.5	236.9	.5
108.0	.8	163.1	1.1	250.9	100.0
109.0	.4	164.0	.7	251.9	15.9
110.9	16.6	165.1	.6	252.9	64.7
111.9	1.3	169.0	.3	253.9	8.2
113.0	5.9	181.1	.5	254.9	11.3
114.0	.7	183.2	.3	255.9	1.4
123.0	.3	185.9	.4	323.9	1.2
124.9	.1	187.1	.4	325.9	.7
126.0	.6	188.1	.5	328.0	.3

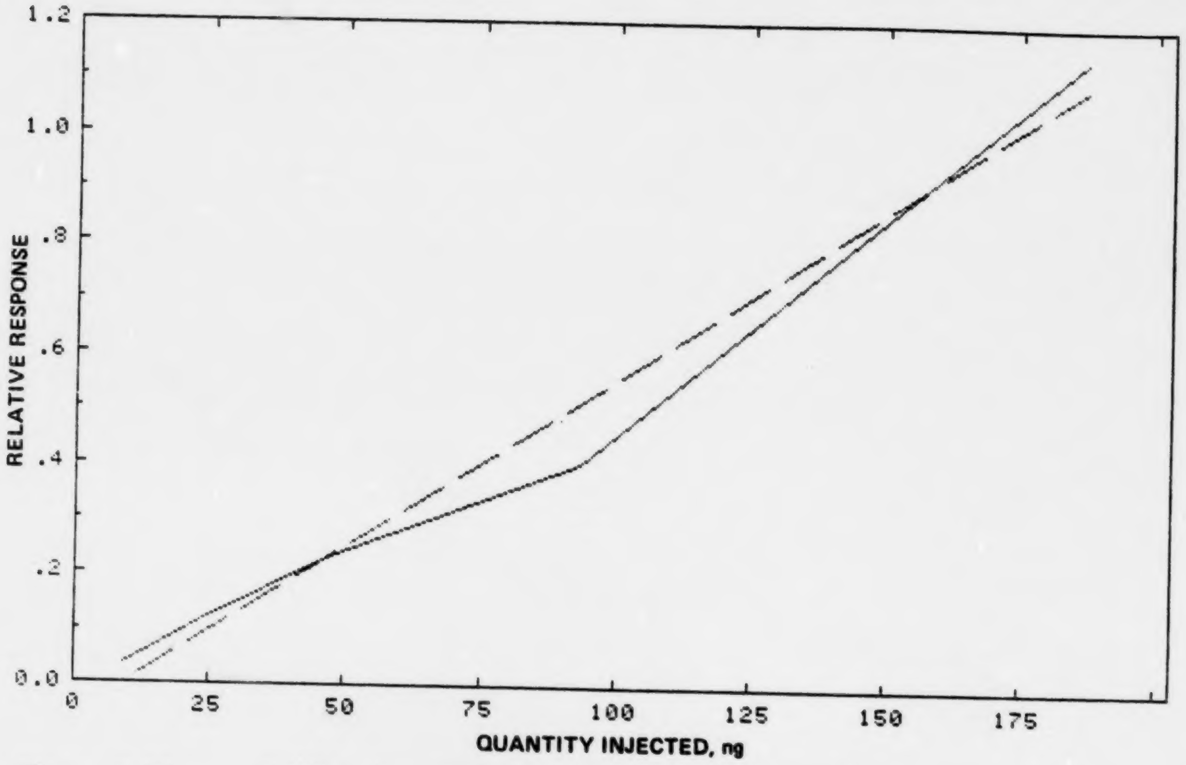


Figure B-90. Calibration curve for the determination of chlorobenzilate by GC/MS.

Range: 47 - 190 ng
Correlation coefficient: 0.989
Slope: 6.1×10^{-3}
y-Intercept: -5.8×10^{-2}

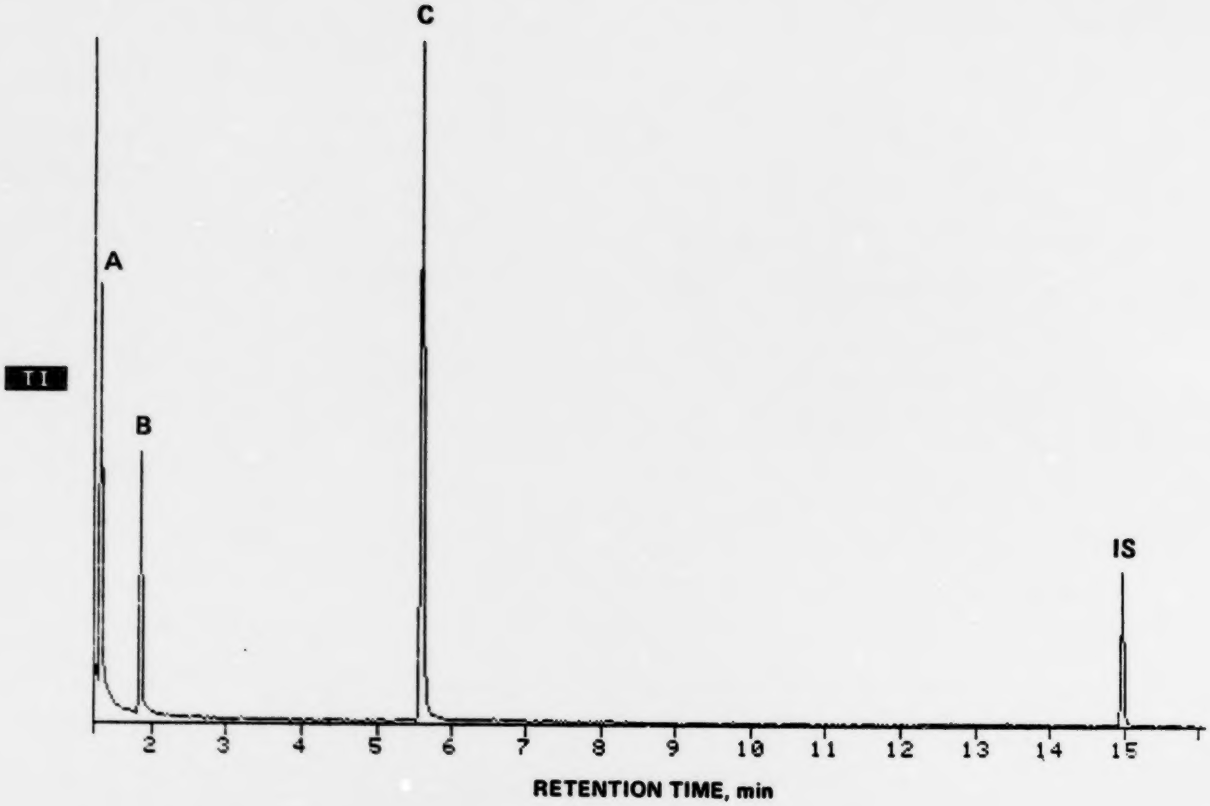


Figure B-91. Chromatogram by GC/MS for

(A) methyl methacrylate(t_R = 1.4 min),
(B) ethyl methacrylate(t_R = 1.9 min), and
(C) m-cresol(t_R = 5.8 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

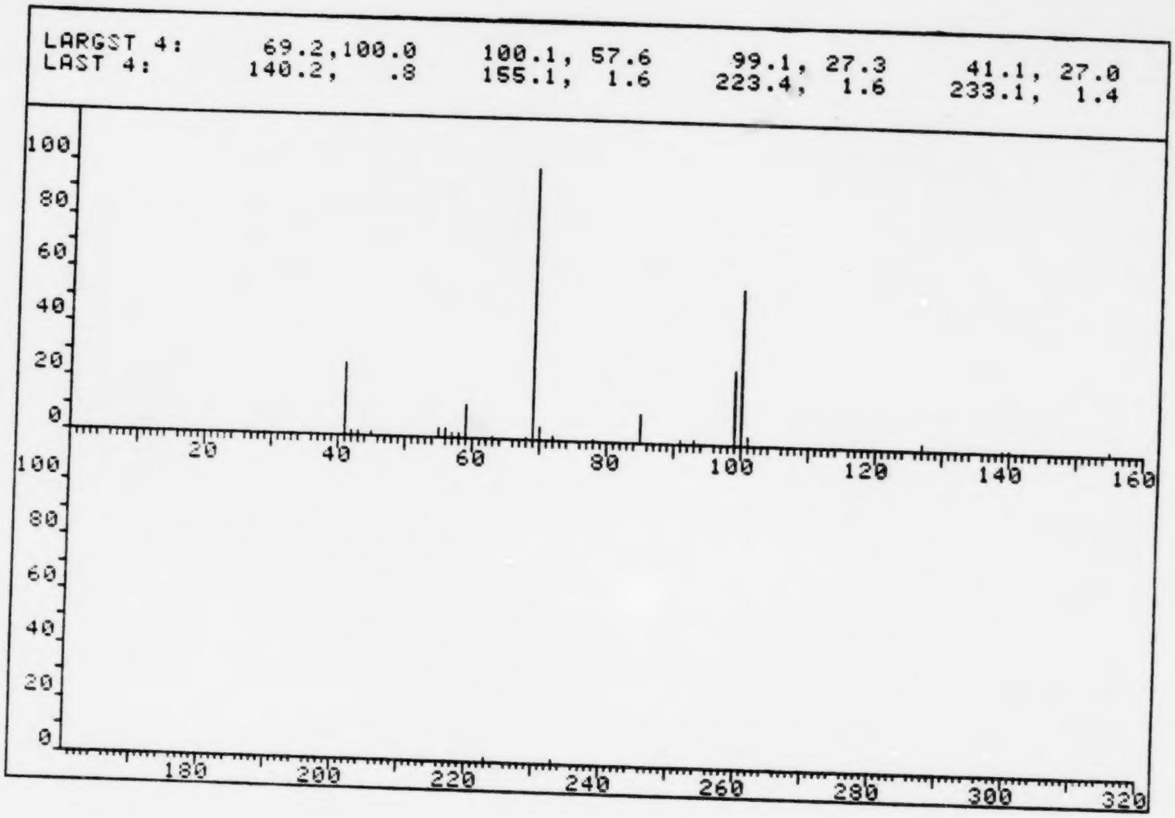


Figure B-92. Mass spectrum for methyl methacrylate.

TABLE B-40. KEY IONS AND RELATIVE ABUNDANCES FOR METHYL METHACRYLATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.1	27.0	63.0	.3	99.1	27.3
42.1	1.4	68.0	1.1	100.1	57.6
43.1	1.6	69.2	100.0	101.2	3.5
45.1	1.4	70.1	4.9	127.1	2.4
55.1	3.0	72.1	1.4	139.2	.3
56.2	3.5	78.1	.3	140.2	.8
57.1	1.4	85.1	10.3	155.1	1.6
58.2	1.9	91.1	1.4	223.4	1.6
59.1	11.9	93.6	1.6	233.1	1.4

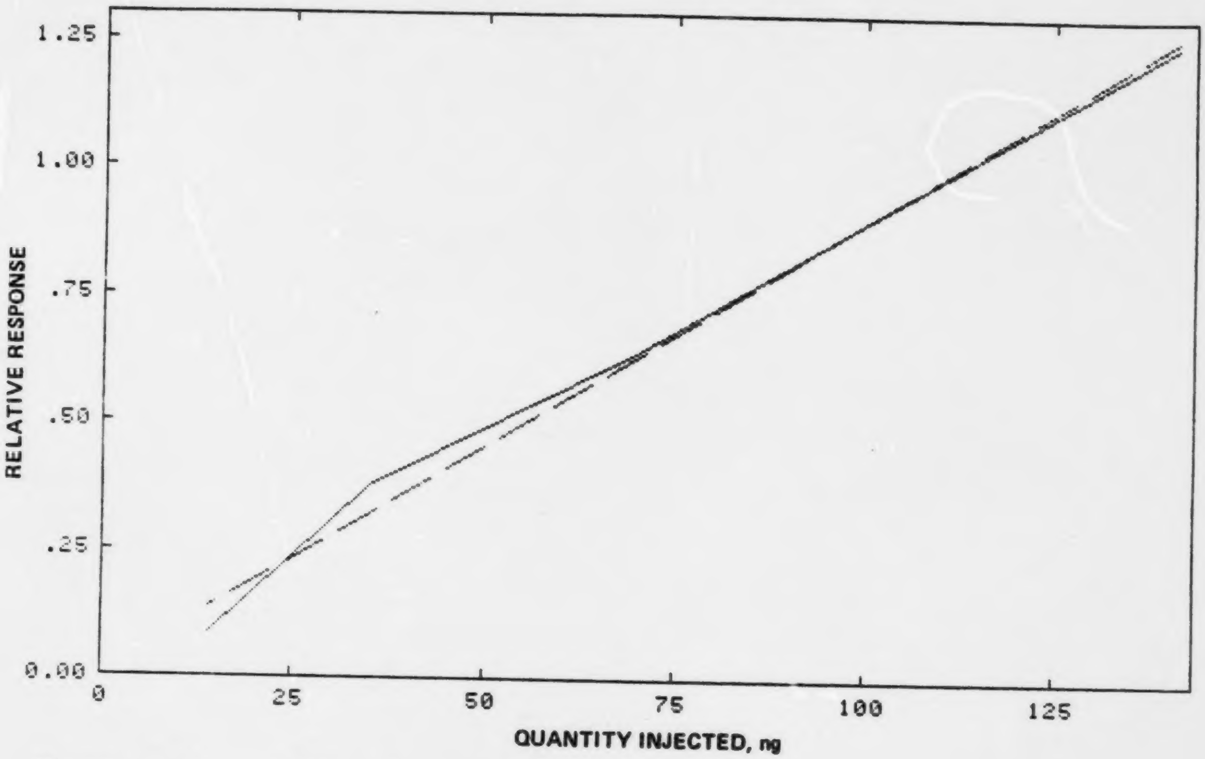


Figure B-93. Calibration curve for the determination of methyl methacrylate by GC/MS.

Range: 35 - 140 ng
Correlation coefficient: 0.996
Slope: 8.9×10^{-3}
y-Intercept: 9.6×10^{-3}

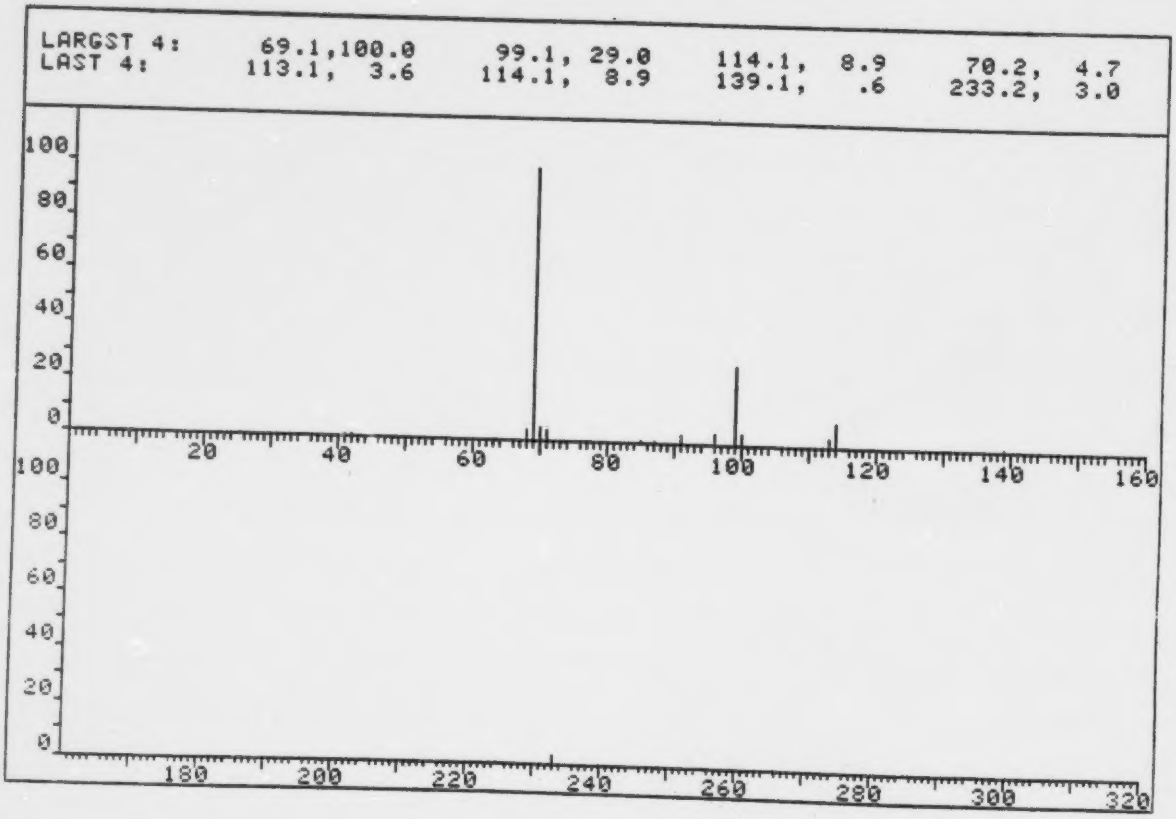


Figure B-94. Mass spectrum for ethyl methacrylate.

TABLE B-41. KEY IONS AND RELATIVE ABUNDANCES FOR ETHYL METHACRYLATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.1	1.2	85.0	.6	100.1	4.1
42.1	.6	87.1	1.2	113.1	3.6
68.1	4.1	91.2	3.6	114.1	8.9
69.1	100.0	96.1	4.1	139.1	.6
70.2	4.7	99.1	29.0	233.2	3.0
71.1	4.1				

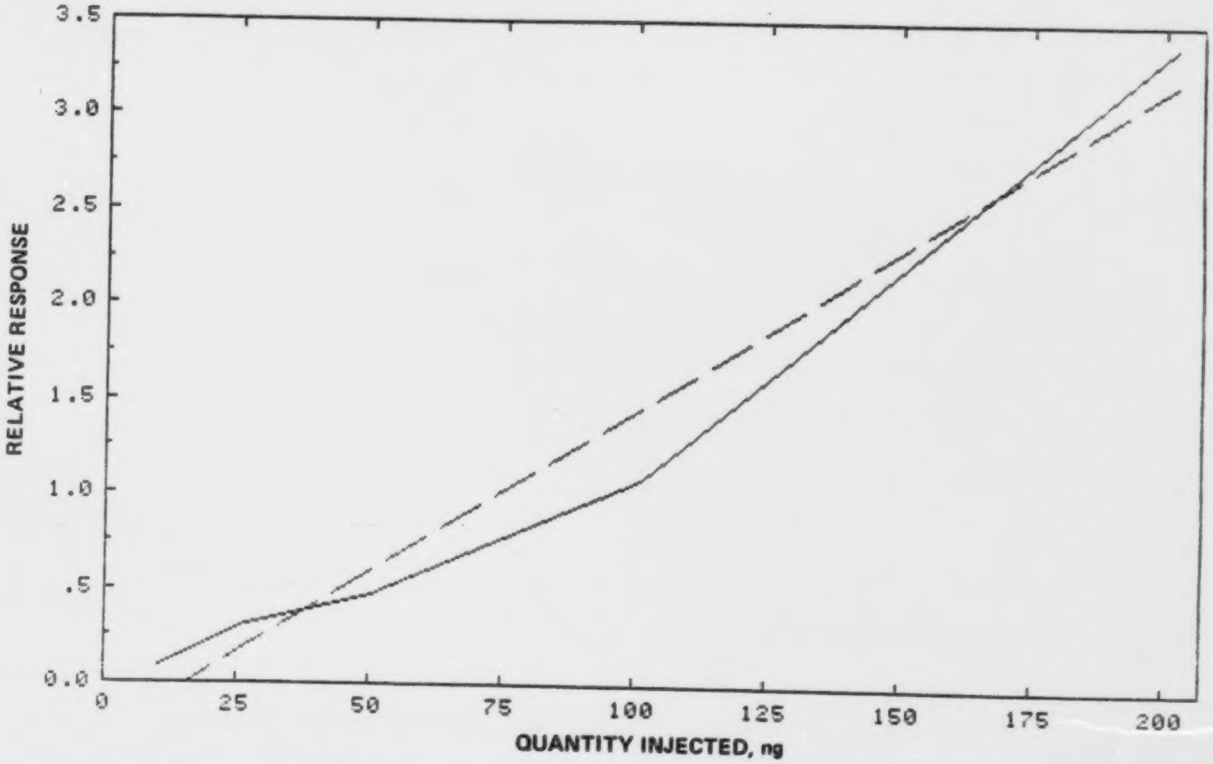
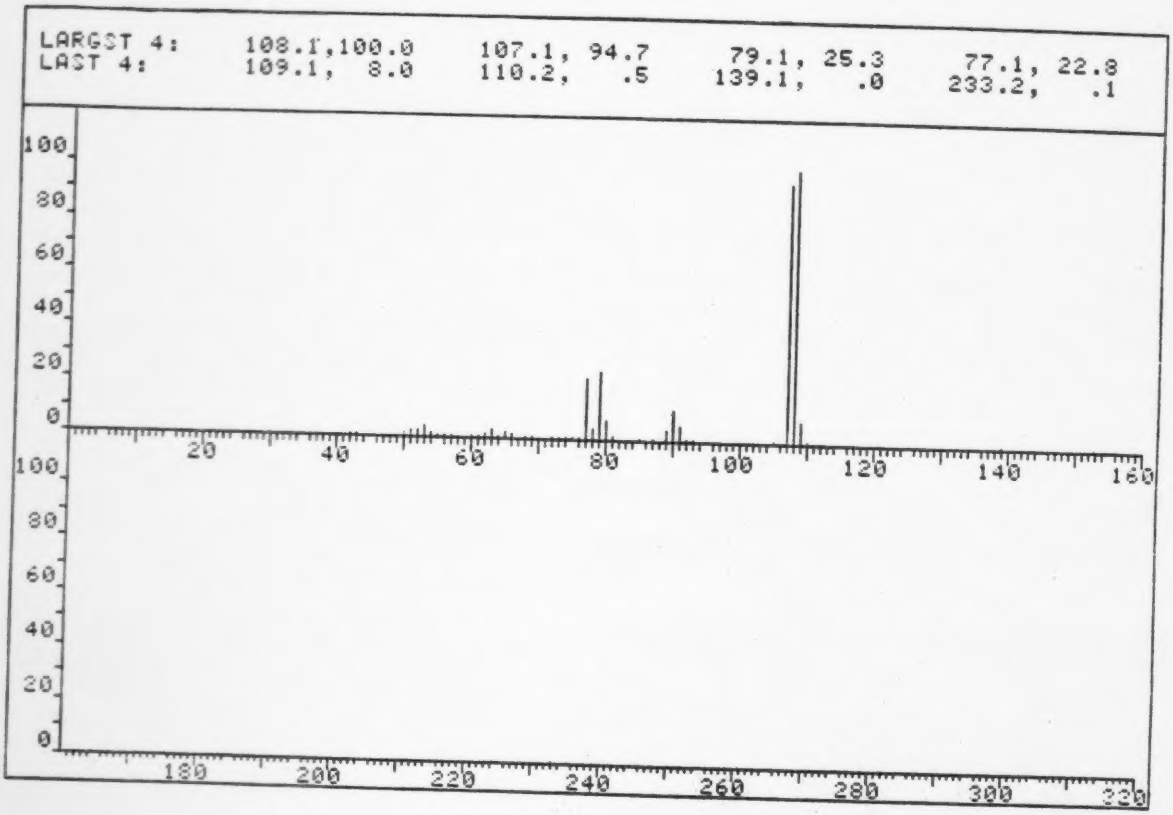


Figure B-95. Calibration curve for the determination of ethyl methacrylate by GC/MS.

Range: 50 - 200 ng
Correlation coefficient: 0.983
Slope: 1.7 x 10^{-2}
y-Intercept: -2.6 x 10^{-1}



```
LARGST 4:     108.1,100.0     107.1, 94.7      79.1, 25.3      77.1, 22.8
LAST 4:       109.1,  8.0     110.2,   .5     139.1,   .0     233.2,   .1
```

Figure B-96. Mass spectrum for m-cresol.

TABLE B-42. KEY IONS AND RELATIVE ABUNDANCES m-CRESOL

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
42.2	.1	65.2	2.3	85.1	.1
43.1	.4	66.1	1.7	87.1	.1
50.1	1.8	68.1	.6	89.1	4.5
51.1	2.3	69.2	.3	90.1	11.4
52.1	2.1	72.2	.1	91.1	5.8
53.1	4.1	73.1	.4	92.2	.6
54.1	1.7	74.1	1.1	93.1	.2
55.1	1.3	75.2	.5	105.1	.8
56.2	.1	76.1	.4	107.1	94.7
57.1	.1	77.1	22.8	108.1	100.0
60.0	.1	78.1	4.5	109.1	8.0
61.1	.7	79.1	25.3	110.2	.5
62.1	1.9	80.1	7.4	139.1	.0
63.1	3.5	81.1	1.4	233.2	.1
64.1	1.0				

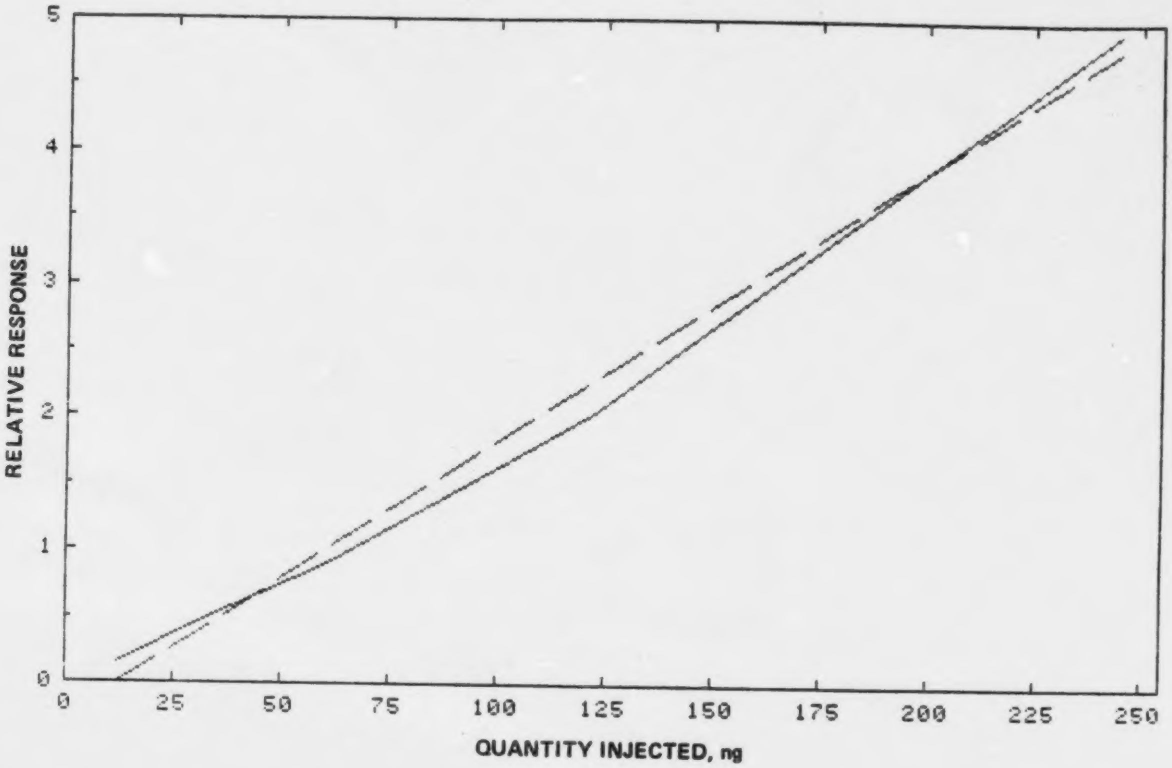


Figure B-97. Calibration curve for the determination of m-cresol by GC/MS.

Range: 31 - 240 ng
Correlation coefficient: 0.996
Slope: 2.1×10^{-2}
y-Intercept: -2.4×10^{-1}

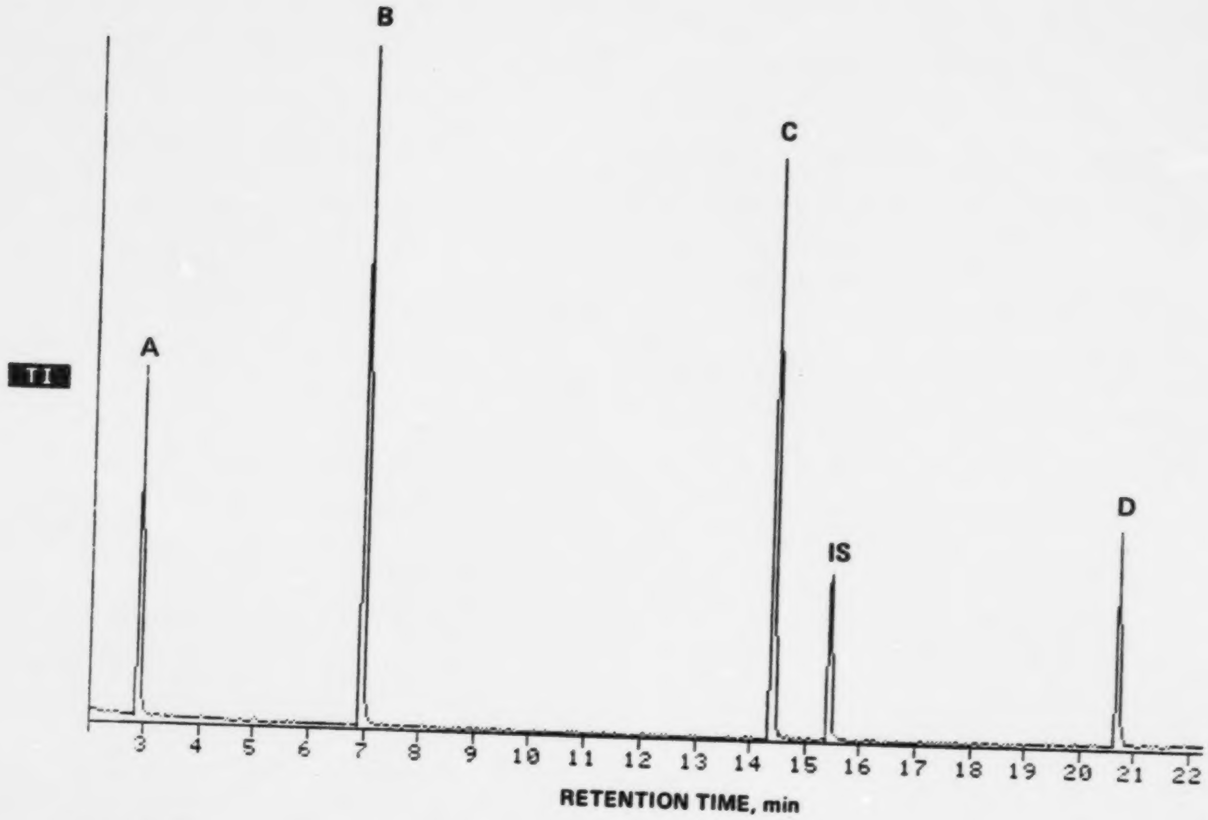


Figure B-98. Chromatogram by GC/MS for

(A) methyl methanesulfonate(t_R = 2.7 min),
(B) (dichloromethyl)benzene(t_R = 6.7 min),
(C) phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester(t_R = 14.3 min), and
(D) phosphorothioic acid, O,O-diethyl o-(p-((dimethylamino)sulfonyl)phenyl) ester t_R = 20.6 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal

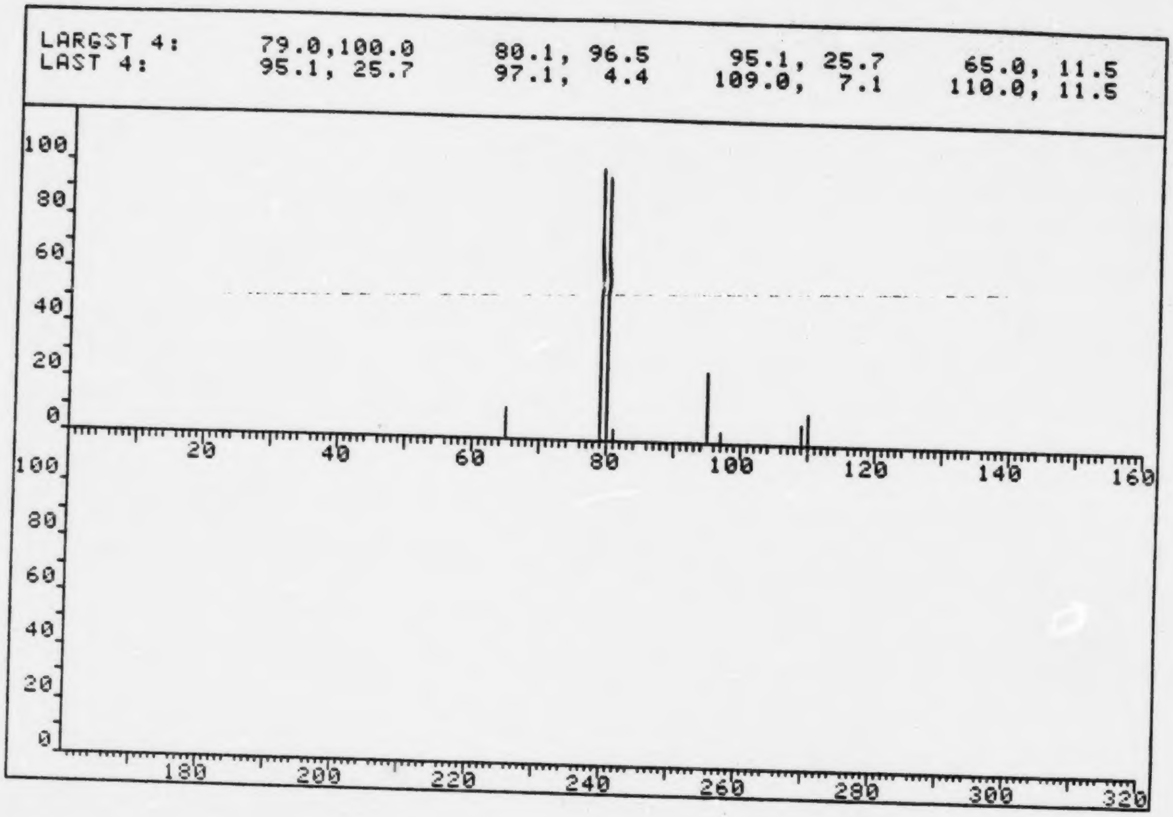


Figure B-99. Mass spectrum for methyl methanesulfonate.

TABLE B-43. KEY IONS AND RELATIVE ABUNDANCES FOR METHYL METHANESULFONATE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
65.0	11.5	81.1	4.4	109.0	7.1
79.0	100.0	95.1	25.7	110.0	11.5
80.1	96.5	97.1	4.4		

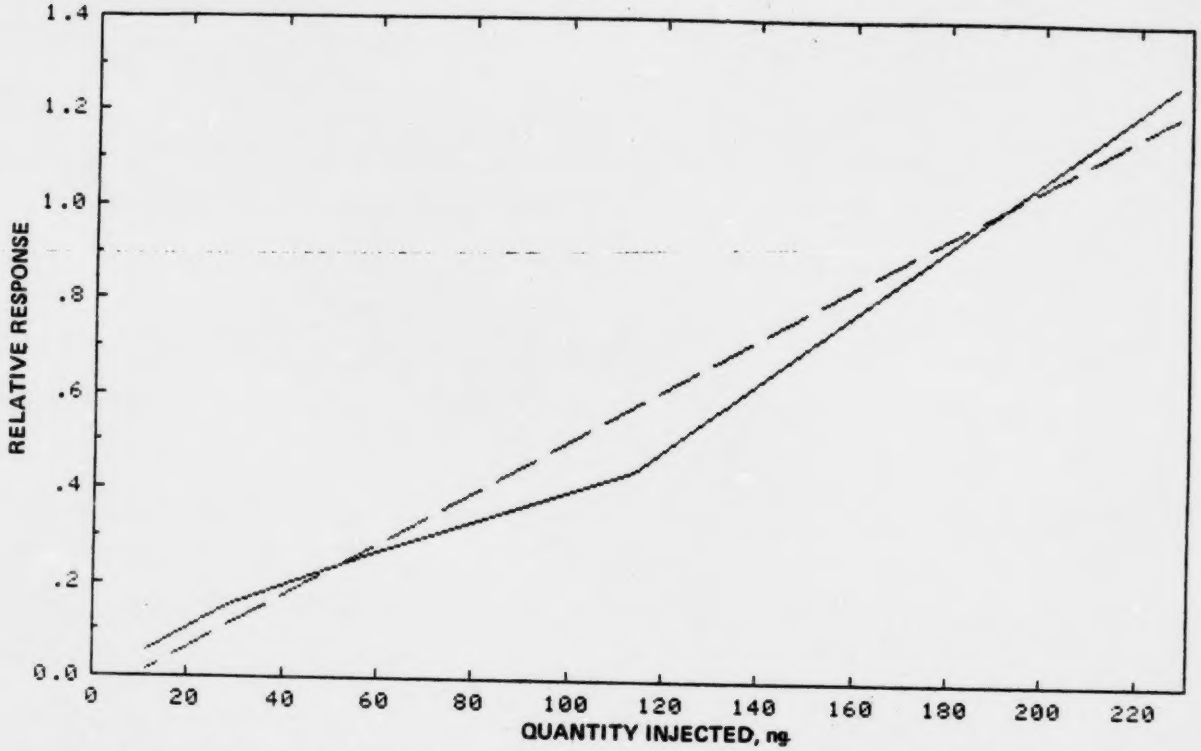
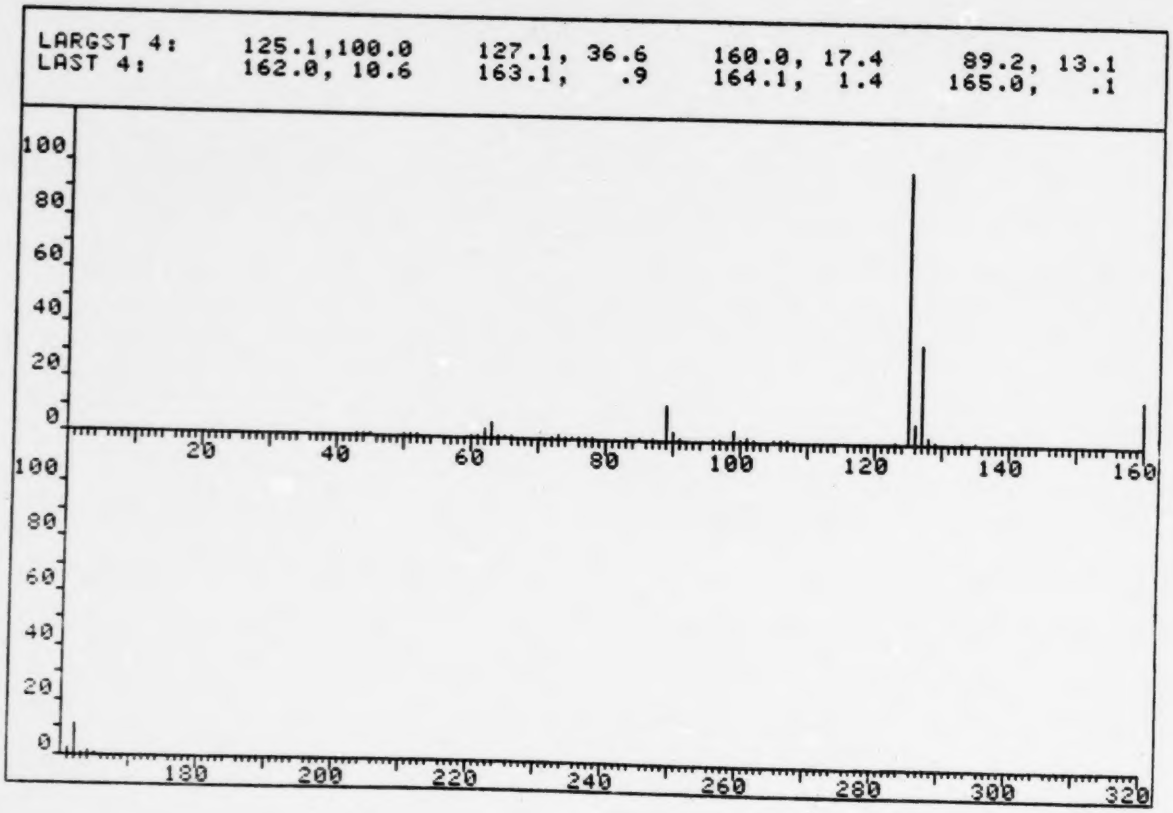


Figure B-100. Calibration curve for the determination of methyl methanesulfonate by GC/MS.

Range: 57 - 230 ng
Correlation coefficient: 0.986
Slope: 5.5×10^{-3}
y-Intercept: -4.7×10^{-2}



```
LARGST 4:     125.1,100.0     127.1, 36.6     160.0, 17.4      89.2, 13.1
LAST 4:       162.0, 10.6     163.1,    .9    164.1,   1.4    165.0,    .1
```

Figure B-101. **Mass spectrum for (dichloromethyl)benzene.**

TABLE B-44. KEY IONS AND RELATIVE ABUNDANCES FOR (DICHLOROMETHYL)BENZENE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
43.2	.3	76.1	.1	106.2	.9
44.1	.0	77.1	.9	107.1	.3
44.7	.6	78.1	.1	123.1	.5
50.1	.6	83.0	.1	125.1	100.0
51.1	.0	85.1	.7	126.1	7.4
52.2	.0	87.1	.7	127.1	36.6
59.8	.1	89.2	13.1	128.1	2.5
61.1	1.0	90.2	2.8	129.1	.2
62.2	3.4	91.2	.3	133.1	.2
63.1	5.8	96.1	.1	135.0	.2
64.0	.7	97.2	.7	160.0	17.4
65.1	.5	99.1	4.0	161.1	1.8
66.2	.0	100.2	.2	162.0	10.6
72.0	.1	101.2	1.4	163.1	.9
73.1	1.6	102.2	.1	164.1	1.4
74.1	.6	105.1	.9	165.0	.1
75.1	1.3				

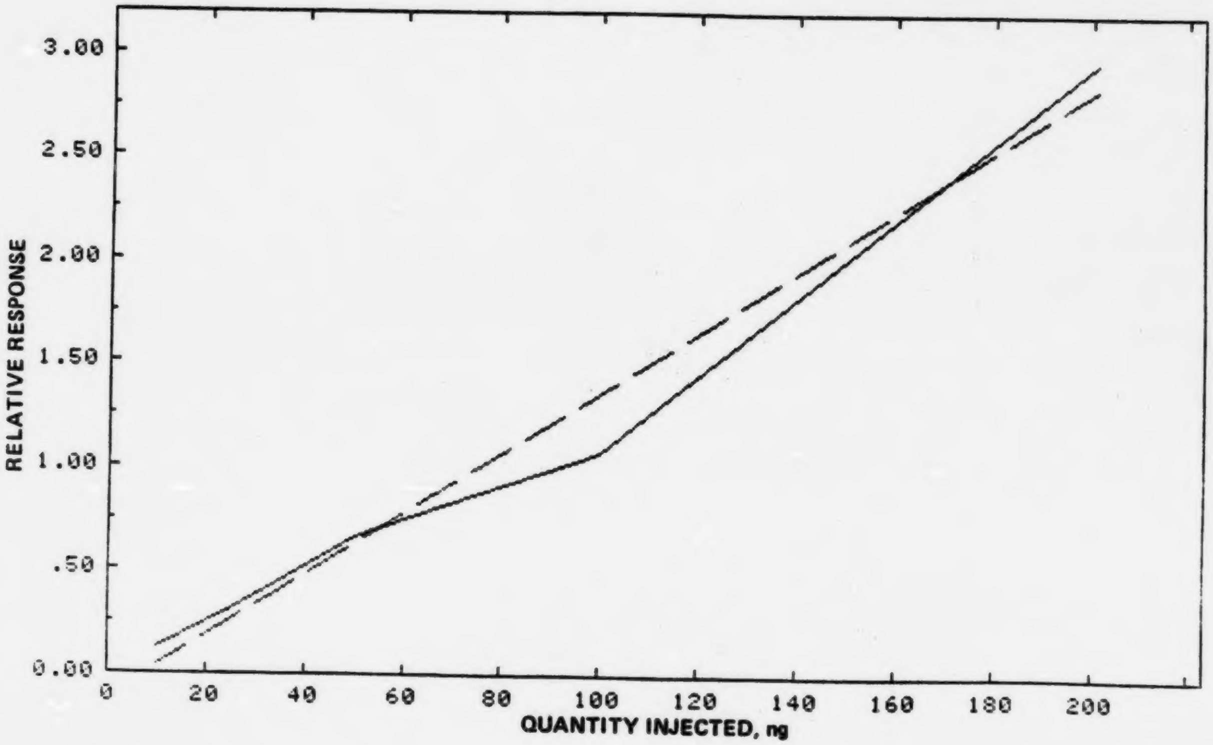


Figure B-102. Calibration curve for the determination of (dichloromethyl)benzene by GC/MS.

Range: 25 - 200 ng
Correlation coefficient: 0.989
Slope: 1.5×10^{-2}
y-Intercept: -1.0×10^{-1}

TABLE B-45. KEY IONS AND RELATIVE ABUNDANCES FOR PHOSPHORODITHIOIC ACID, O,O-DIETHYL S-((ETHYLTHIO)METHYL) ESTER

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
41.4	1.5	108.0	1.0	158.9	2.7
44.9	1.0	109.2	2.7	171.1	1.5
59.1	1.3	111.9	2.3	172.0	2.5
60.0	1.0	113.0	3.8	175.0	4.6
61.1	1.7	115.2	.2	176.9	1.0
63.0	2.1	121.1	59.5	185.0	4.2
75.0	8.6	122.1	2.7	186.0	5.2
74.1	4.0	123.2	1.7	187.1	4.4
75.1	92.7	124.0	1.0	188.1	1.3
76.1	5.7	125.1	16.4	189.0	1.0
77.1	1.7	127.1	2.7	199.1	2.3
78.1	.2	129.1	13.2	200.1	2.9
79.1	4.0	130.0	1.0	202.2	1.5
80.0	1.5	130.5	2.7	203.0	7.1
81.0	.8	141.1	3.4	215.0	1.9
91.0	1.5	143.1	1.9	231.0	45.5
93.2	10.0	144.0	1.7	232.0	3.8
94.0	.8	153.1	10.1	233.0	7.1
95.0	1.5	154.1	6.9	260.1	100.0
97.0	30.2	155.1	5.2	261.1	9.6
99.1	2.3	156.1	3.6	262.1	11.9
06.2	1.5	157.0	4.8	263.1	1.9
07.0	10.7	157.9	1.3	264.1	1.3

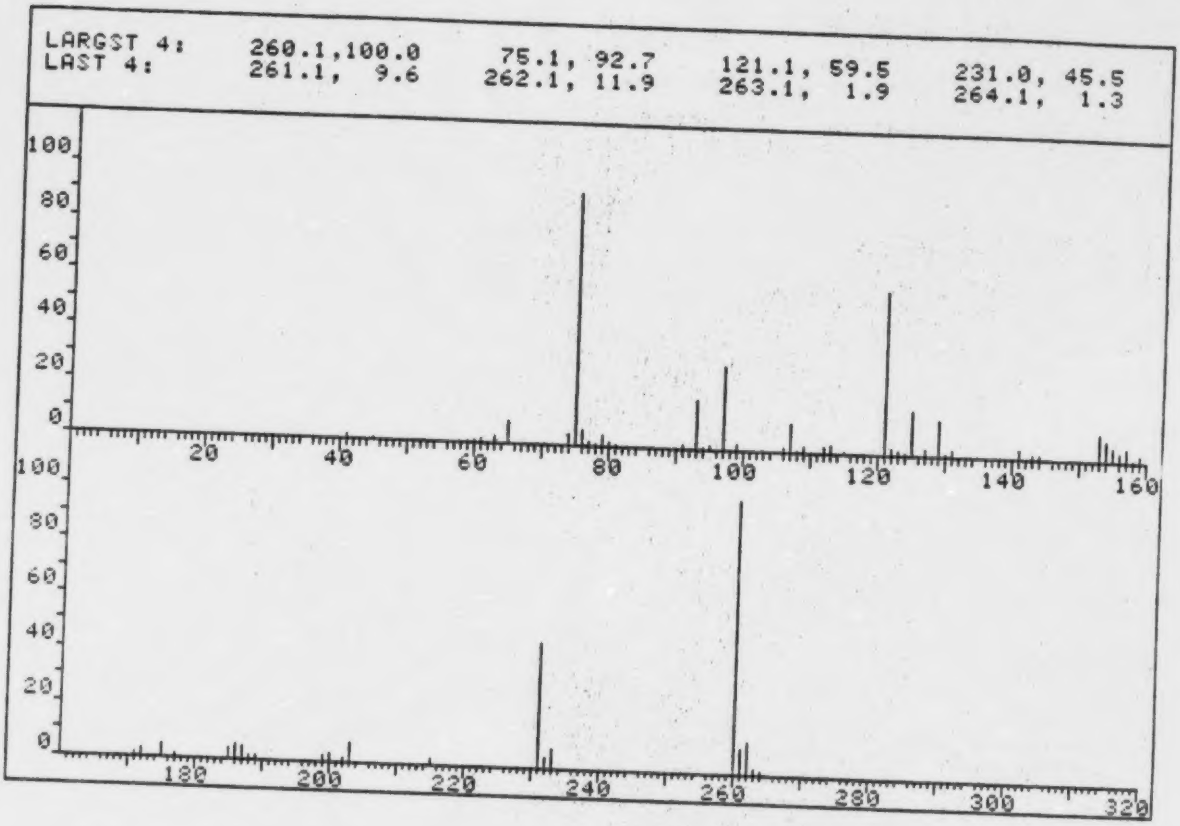


Figure B-103. Mass spectrum for phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester.

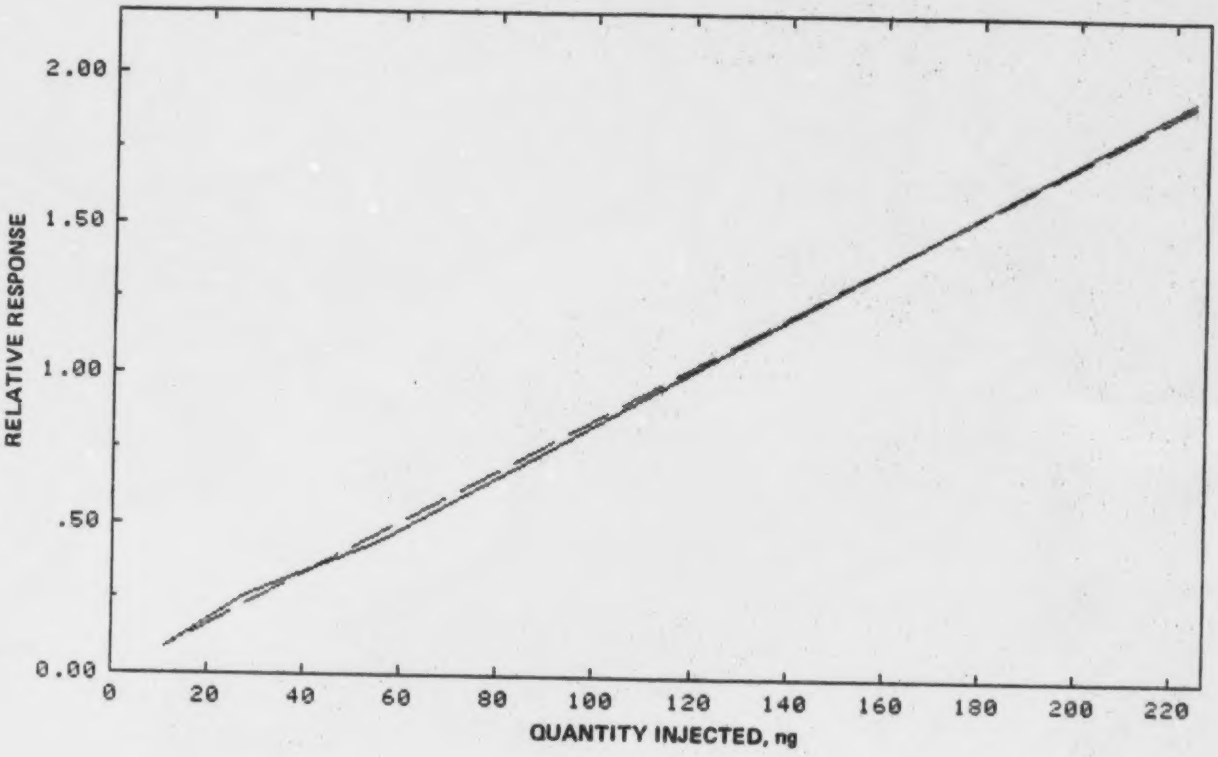
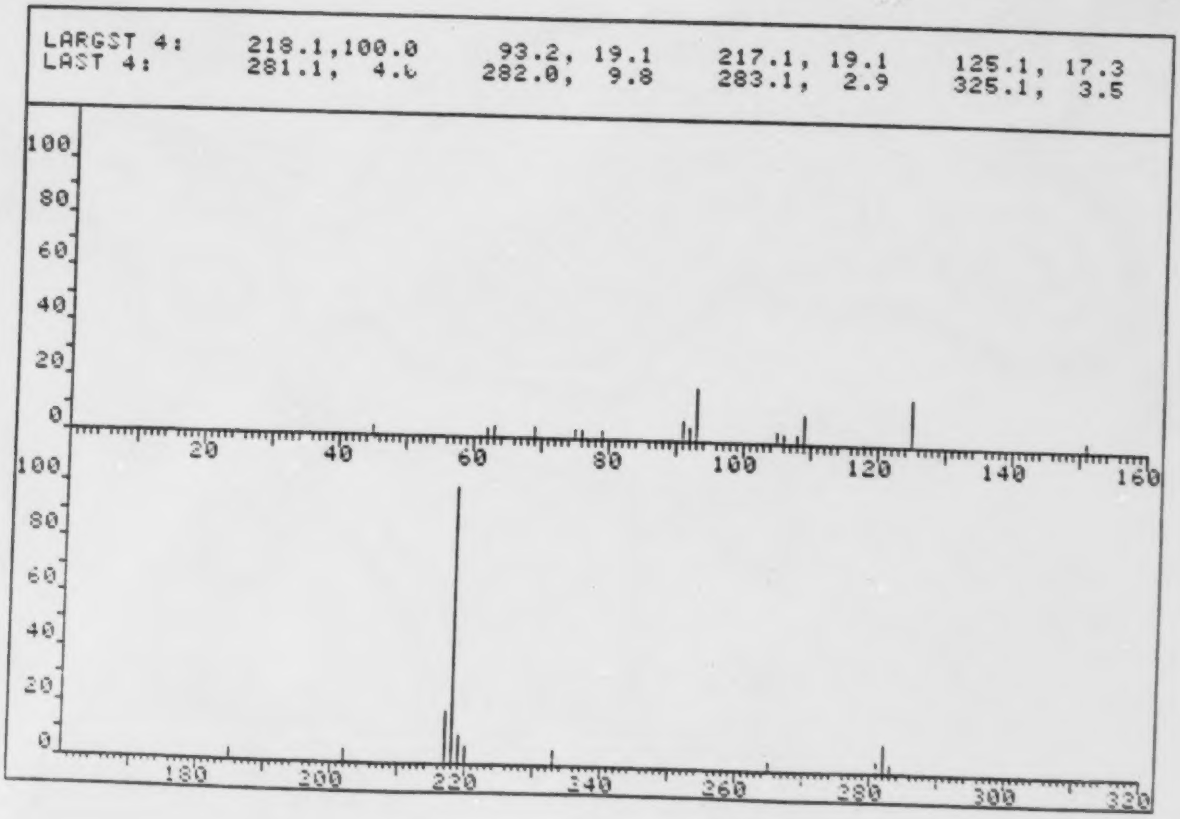


Figure B-104. Calibration curve for the determination of phosphorodithioic acid, O,O-diethyl S-((ethylthio)methyl) ester

Range: 11 - 220 ng
Correlation coefficient: 0.999
Slope: 8.6×10^{-3}
y-Intercept: -1.1×10^{-2}



```
LARGST 4:     218.1,100.0       93.2, 19.1      217.1, 19.1      125.1, 17.3
LAST 4:       281.1,   4.6     282.0,  9.8      283.1,  2.9      325.1,  3.5
```

Figure B-105. Mass spectrum for phosphorothioic acid, *O*,*O*-diethyl *O*-(*p*-((dimethylamino)sulfonyl)phenyl) ester.

TABLE B-46. KEY IONS AND RELATIVE ABUNDANCES FOR PHOSPHOROTHIOIC ACID, *O*,*O*-DIMETHYL *O*-(*p*-((DIMETHYLAMINO)SULFONYL)PHENYL) ESTER

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
45.0	2.9	105.2	4.0	218.1	100.0
62.2	3.5	106.0	3.5	219.1	10.4
63.0	4.0	108.2	2.9	220.1	6.4
69.3	4.0	109.0	10.4	233.0	5.2
75.3	3.5	125.1	17.3	265.0	2.9
76.3	3.5	151.1	3.5	281.1	4.0
79.1	3.5	185.0	4.0	282.0	9.8
91.2	6.9	202.1	4.6	283.1	2.9
92.0	5.2	217.1	19.1	325.1	3.5
93.2	19.1				

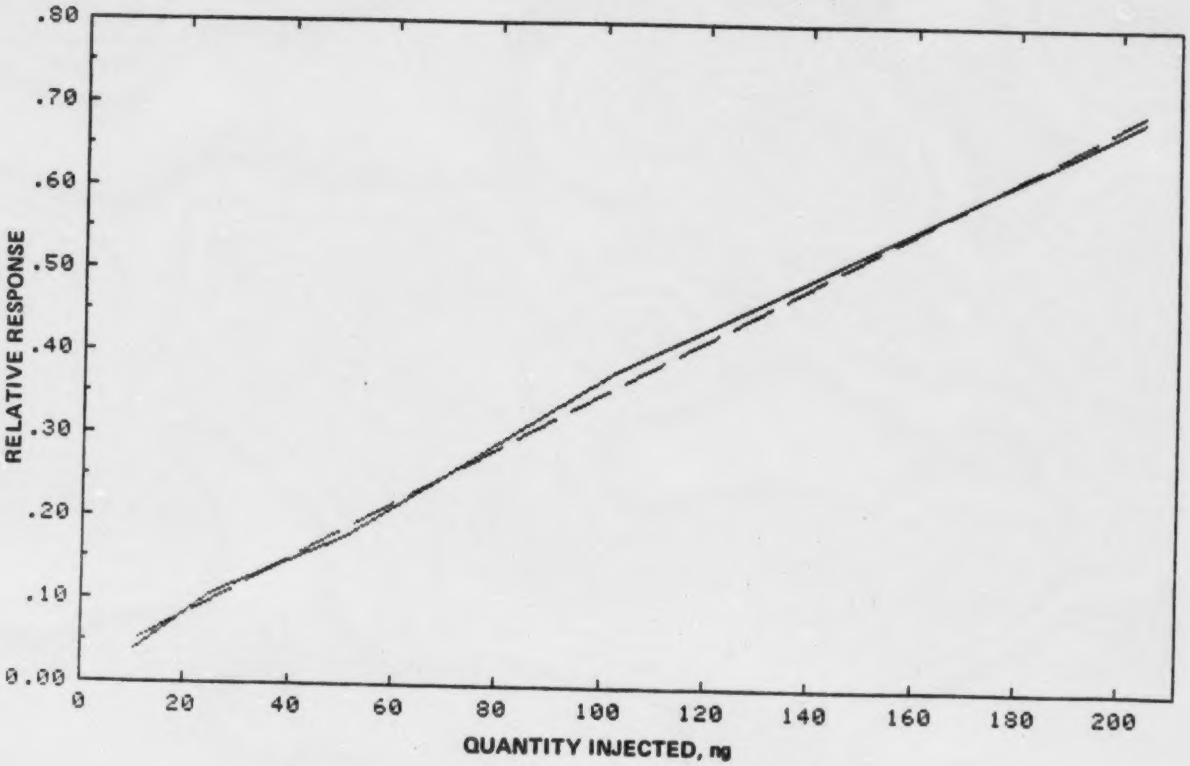


Figure B-106. Calibration curve for the determination of phosphorothioic acid, O,O-diethyl O-(p-((dimethylamino)sulfonyl)phenyl) ester.

Range: 10 - 200 ng
Correlation coefficient: 0.998
Slope: 3.4×10^{-3}
y-Intercept: 1.5×10^{-2}

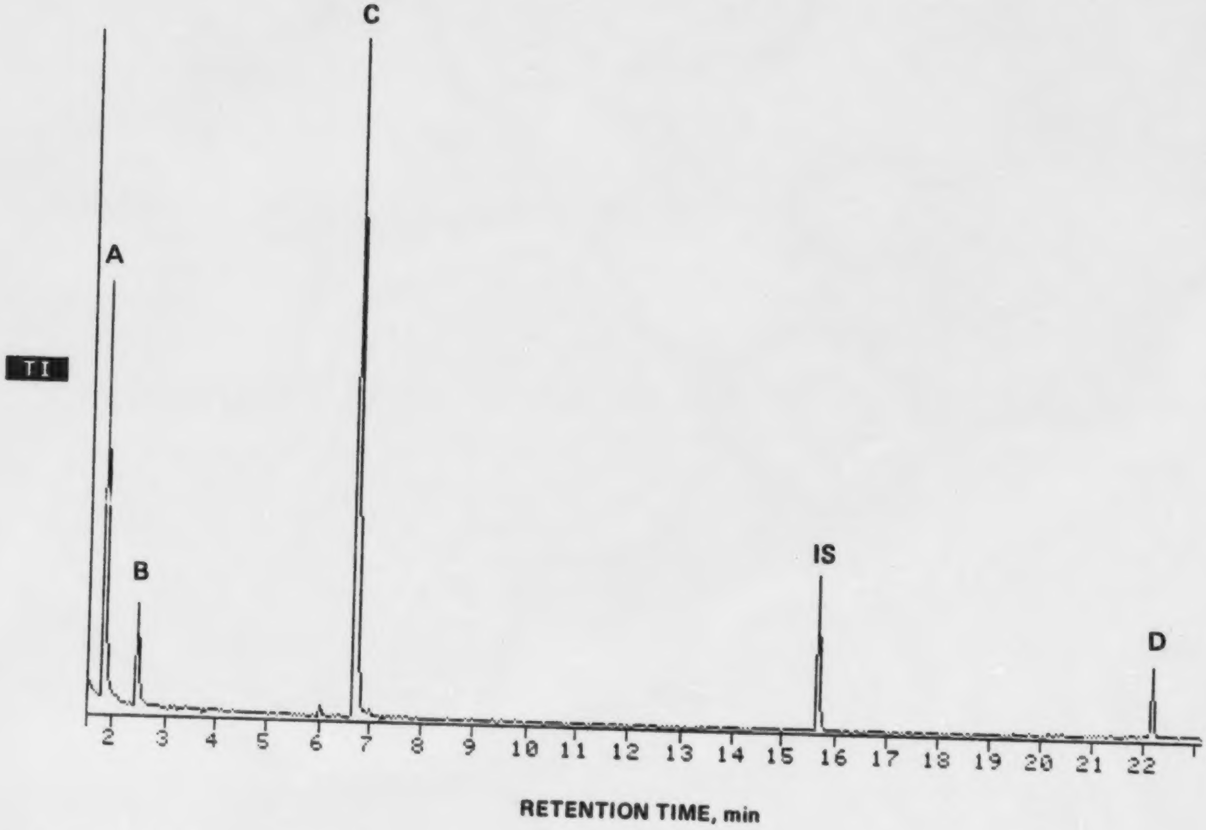
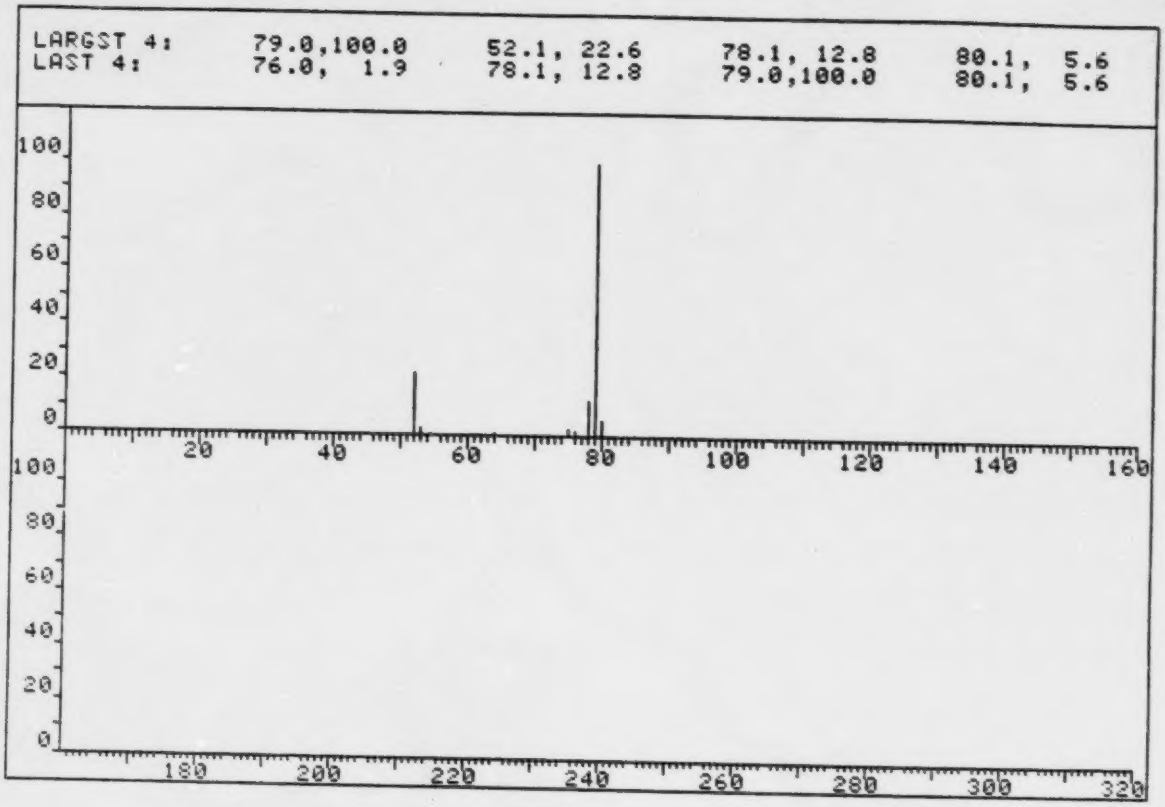


Figure B-107. Chromatogram by GC/MS for

(A) pyridine(t_R = 1.6 min),
(B) 3-chloropropionitrile(t_R = 2.2 min),
(C) α,α-dimethylphenethylamine(t_R = 6.3 min), and
(D) 4,4'-methylenebis(2-chloroaniline)(t_R = 22.0 min).

Temperature program:
40 °C, 0 min isothermal
40 to 280 °C at 10 °C/min
280 °C, 15 min isothermal



```
LARGST 4:      79.0,100.0      52.1, 22.6      78.1, 12.8      80.1,  5.6
LAST 4:        76.0,  1.9      78.1, 12.8      79.0,100.0      80.1,  5.6
```

Figure B-108. **Mass spectrum for pyridine.**

TABLE B-47. KEY IONS AND RELATIVE ABUNDANCES FOR PYRIDINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
52.1	22.6	75.0	2.2	79.0	100.0
53.0	2.0	76.0	1.9	80.1	5.6
64.0	.1	78.1	12.8		

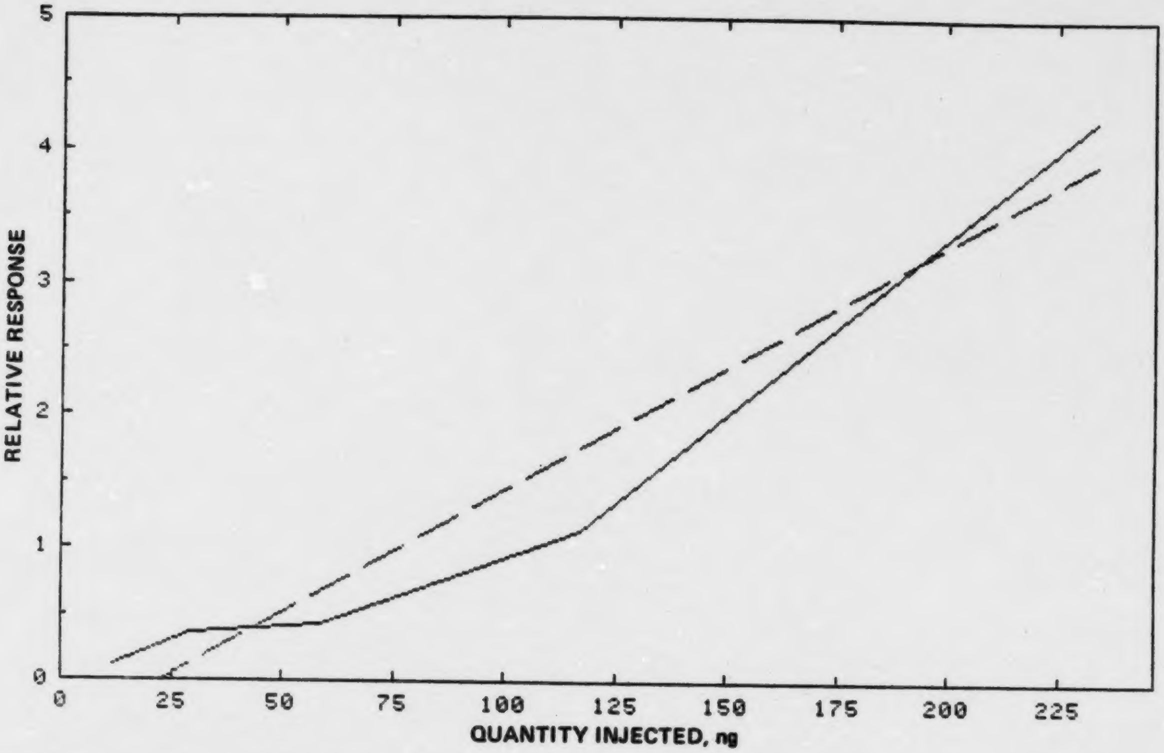
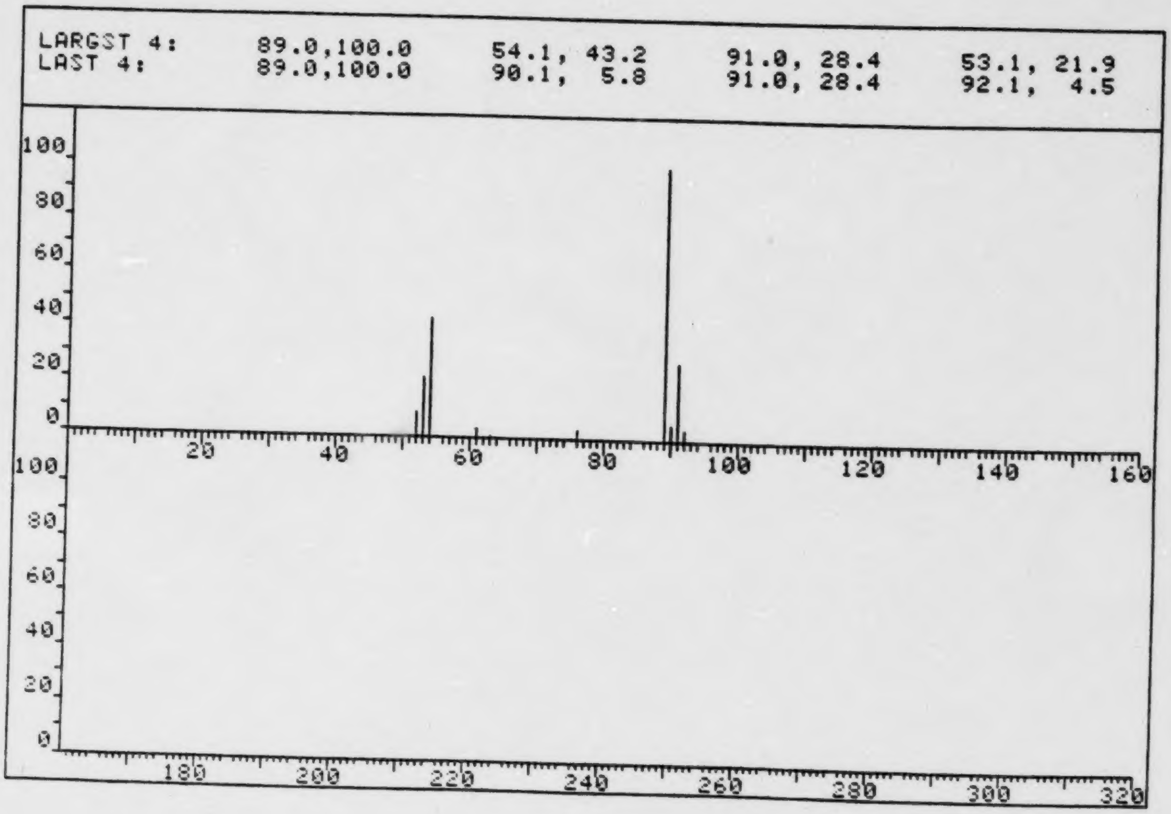


Figure B-109. Calibration curve for the determination of pyridine by GC/MS.

Range: 58 - 230 ng
Correlation coefficient: 0.970
Slope: 1.8×10^{-2}
y-Intercept: -4.0×10^{-1}



```
LARGST 4:     89.0,100.0     54.1, 43.2     91.0, 28.4     53.1, 21.9
LAST 4:       89.0,100.0     90.1,  5.8     91.0, 28.4     92.1,  4.5
```

Figure B-110. Mass spectrum for 3-chloropropionitrile.

TABLE B-48. KEY IONS AND RELATIVE ABUNDANCES FOR 3-CHLOROPROPIONITRILE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
52.1	9.0	63.0	.6	90.1	5.8
53.1	21.9	76.0	3.2	91.0	28.4
54.1	43.2	89.0	100.0	92.1	4.5
60.9	3.9				

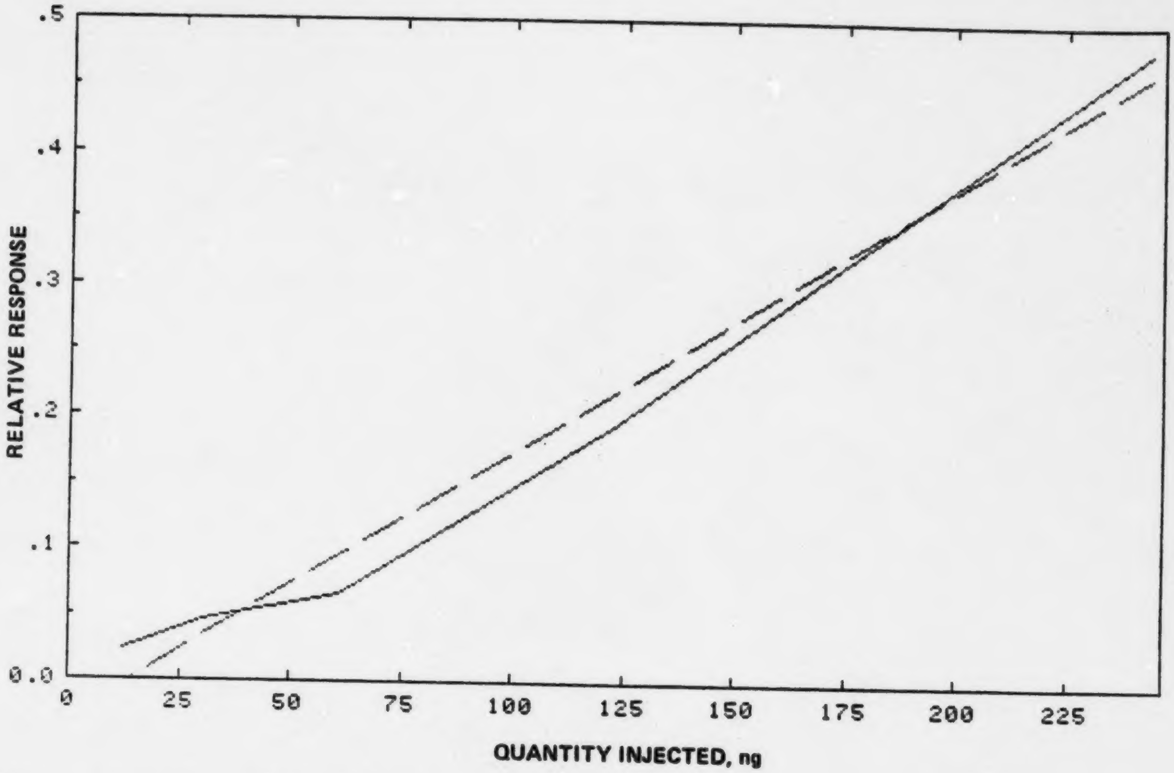


Figure B-111. Calibration curve for the determination of 3-chloropropionitrile by GC/MS.

Range: 61 - 240 ng
Correlation coefficient: 0.991
Slope: 2.0×10^{-3}
y-Intercept: -2.7×10^{-2}

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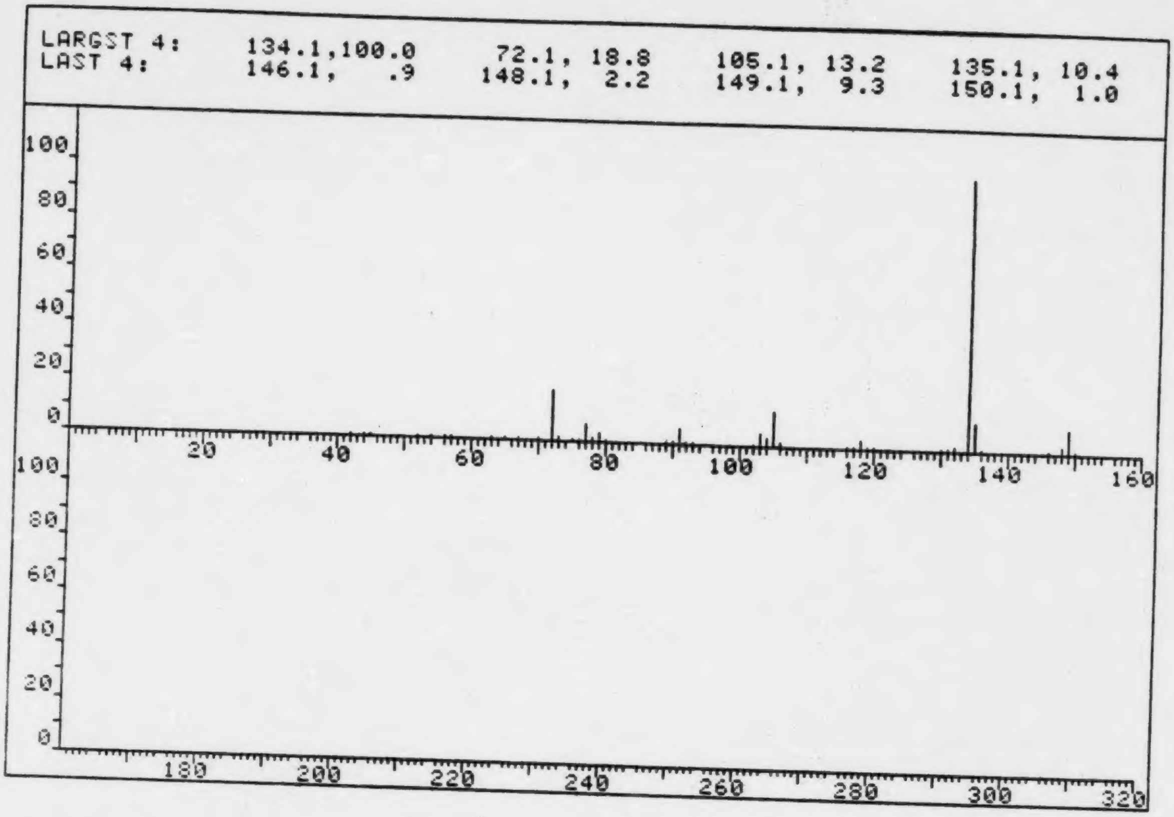


```
LARGST 4:    134.1,100.0      72.1, 18.8     105.1, 13.2     135.1, 10.4
LAST 4:      146.1,    .9    148.1,  2.2     149.1,  9.3     150.1,  1.0
```

Figure B-112. **Mass spectrum for α,α-dimethylphenethylamine.**

TABLE B-49. KEY IONS AND RELATIVE ABUNDANCES FOR α,α-DIMETHYLPHENETHYLAMINE

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
42.1	.2	77.0	6.6	117.1	.6
44.1	.2	78.1	1.7	118.1	3.2
45.2	.2	79.0	3.7	119.1	1.1
51.9	.3	80.0	.4	120.1	.3
54.0	.2	89.0	.8	130.1	.3
56.1	.5	90.0	.4	131.1	.5
57.0	.2	91.0	5.7	132.1	1.5
63.0	.4	92.1	.5	134.1	100.0
65.1	.6	93.2	.2	135.1	10.4
66.7	.9	102.0	1.0	136.0	.4
70.0	.1	103.0	4.7	146.1	.9
72.1	18.8	104.0	3.0	148.1	2.2
73.1	1.4	105.1	13.2	149.1	9.3
75.1	.3	106.0	1.6	150.1	1.0
76.1	.6	116.1	.4		

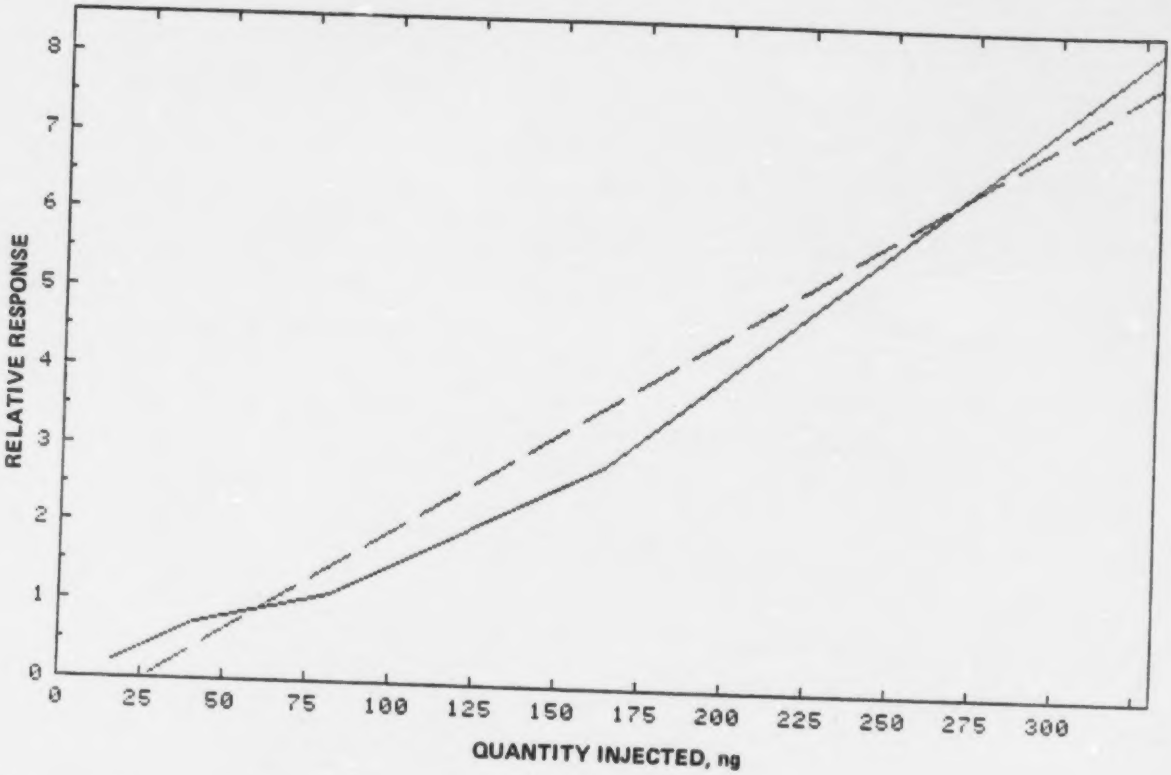
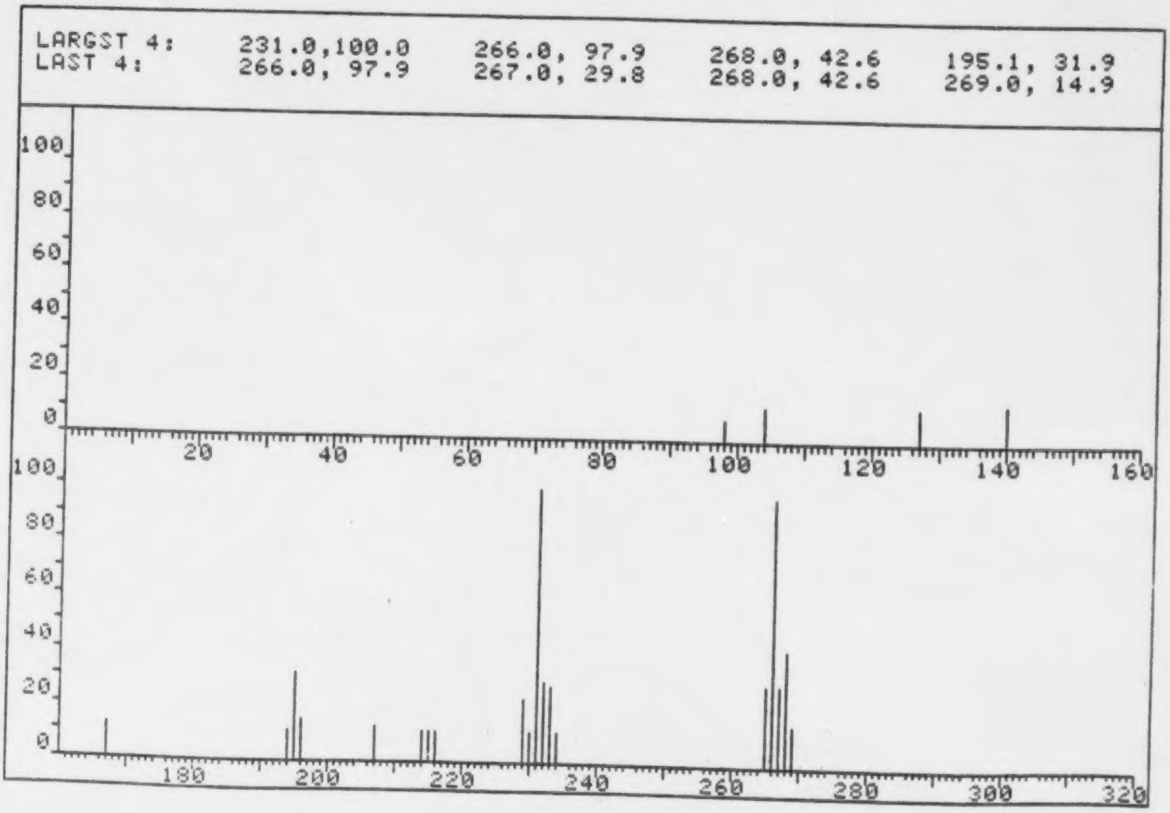


Figure B-113. Calibration curve for the determination of α,α-dimethylphenethylamine by GC/MS.

Range: 82 - 330 ng
Correlation coefficient: 0.987
Slope: 2.6×10^{-2}
y-Intercept: -6.3×10^{-1}



```
LARGST 4:    231.0,100.0    266.0, 97.9    268.0, 42.6    195.1, 31.9
LAST 4:      266.0, 97.9    267.0, 29.8    268.0, 42.6    269.0, 14.9
```

Figure B-114. Mass spectrum for 4,4'-methylenebis(2-chloroaniline).

TABLE B-50. KEY IONS AND RELATIVE ABUNDANCES
4,4'-METHYLENEBIS(2-CHLOROANILINE)

M/Z	Abundance	M/Z	Abundance	M/Z	Abundance
97.9	8.5	206.8	12.8	233.1	27.7
104.0	12.8	214.0	10.6	234.0	10.6
126.9	12.8	215.0	10.6	265.1	29.8
140.1	14.9	216.0	10.6	266.0	97.9
167.2	12.8	229.0	23.4	267.0	29.8
194.2	10.6	230.0	10.6	268.0	42.6
195.1	31.9	231.0	100.0	269.0	14.9
196.1	14.9	232.1	29.8		

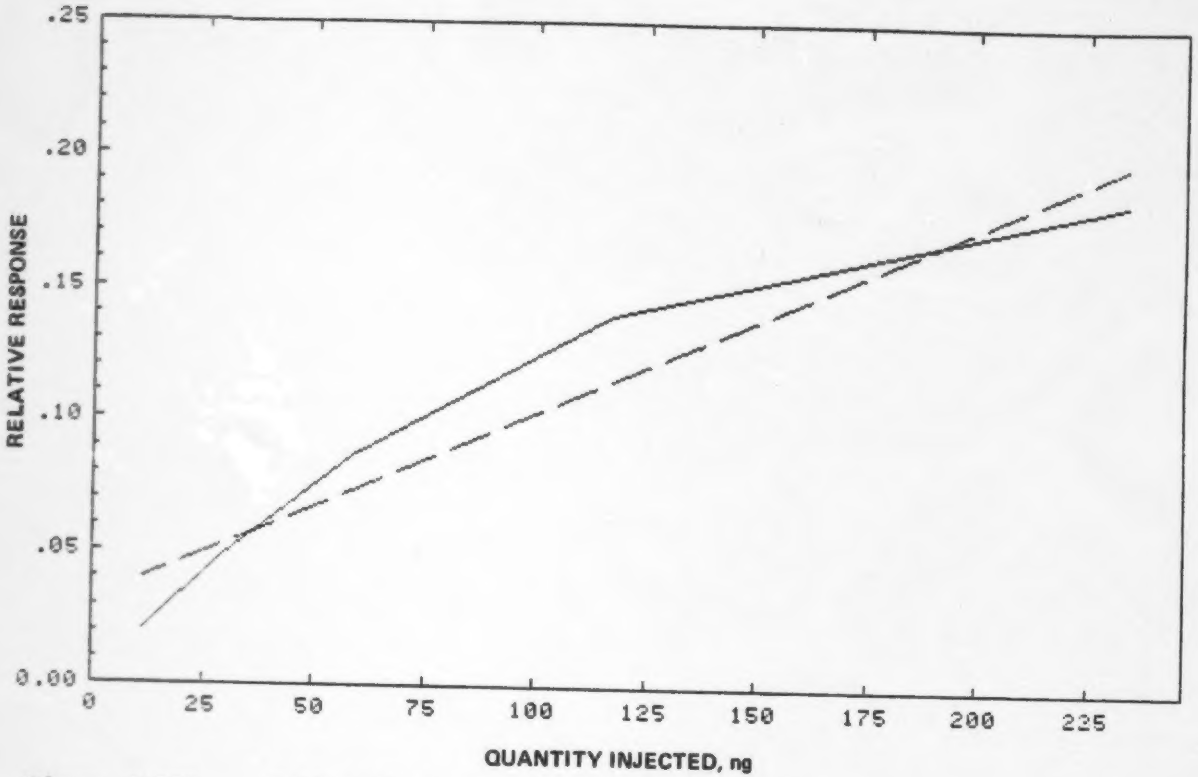


Figure B-115. Calibration curve for the determination of 4,4'-methylenebis(2-chloroaniline) by GC/MS.

Range: 29 - 230 ng
Correlation coefficient: 0.960
Slope: 7.1 x 10^{-4}
y-Intercept: 3.2 x 10^{-2}

APPENDIX C

CHROMATOGRAMS, UV SPECTRA, AND CALIBRATION CURVES FOR HPLC/UV DETERMINATIONS

Index

Compound	Reference chromatogram Figure No.	Reference UV Figure No.	Reference calibration curve Figure No.
Acetaldehyde-DNPH	C-50	C-53	C-54
1-Acetyl-2-thiourea	C-84	C-87	C-88
Azaserine	C-94	C-95	C-96
Benzaldehyde-DNPH	C-45	C-48	C-49
Benzenethiol	C-40	C-43	C-44
Benzidine	C-65	C-66	C-67
Brucine	C-112	C-115	C-116
Chloroacetaldehyde-DNPH	C-57	C-58	C-59
1-(2-Chlorophenyl)thiourea	C-105	C-108	C-109
Crotonaldehyde-DNPH	C-50	C-55	C-56
Daunomycin	C-117	C-120	C-121
3,3'-Dichlorobenzidine	C-72	C-75	C-76
2,6-Dichlorophenol	C-13, C-14	C-18	C-19, C-20
Diethylstilbestrol	C-6	C-11	C-12
3,3'-Dimethoxybenzidine	C-72	C-73	C-74
3,3'-Dimethylbenzidine	C-65	C-68	C-69
2,4-Dimethylphenol	C-21, C-22	C-26	C-27
4,6-Dinitro-*o*-cresol	C-60	C-63	C-64
2,4-Dinitrophenol	C-60	C-61	C-62
Epinephrine	C-99	C-100	C-101
Ethylene thiourea	C-89	C-92	C-93
Formaldehyde-DNPH	C-50	C-51	C-52
Maleic anhydride	C-1	C-2	C-3
Melphalan	C-45	C-46	C-47
Methapyrilene	C-124	C-129	C-130
4,4'-Methylene-bis(2-chloroaniline)	C-65 C-117	C-70, C-122	C-71, C-123
N-Methyl-*N*'-nitro-*N*-nitrosoguanidine	C-6	C-7	C-8
2-Methylphenol	C-29, C-30	C-31	C-32, C-33
3-Methylphenol	C-13, C-14	C-15, C-16	C-17
4-Methylphenol	C-21, C-22	C-23, C-24	C-25
Mitomycin C	C-131	C-132	C-133

(continued)

APPENDIX C INDEX
(continued)

Compound	Reference chromatogram Figure No.	Reference UV Figure No.	Reference calibration curve Figure No.
1-Naphthyl-2-thiourea	C-105	C-110	C-111
Nicotine	C-124	C-125	C-126
4-Nitroquinoline-1-oxide	C-6	C-9	C-10
Pentachlorophenol	C-29, C-30	C-37	C-38,C-39
Phenacetin	C-40	C-41	C-42
Phenylthiourea	C-105	C-106	C-107
Phthalic anhydride	C-1	C-4	C-5
Resorcinol	C-94	C-97	C-98
Saccharin	C-112	C-113	C-114
Streptozotocin	C-117	C-118	C-119
Strychnine	C-124	C-127	C-128
Thioacetamide	C-102	C-103	C-104
Thiosemicarbazide	C-89	C-90	C-91
Thiourea	C-84	C-85	C-86
_o_-Toluidine	C-77	C-78	C-79
2,4,5-Trichlorophenol	C-29. C-30	C-34	C-35, C-36
Trypan Blue	C-80	C-81, C-82	C-83

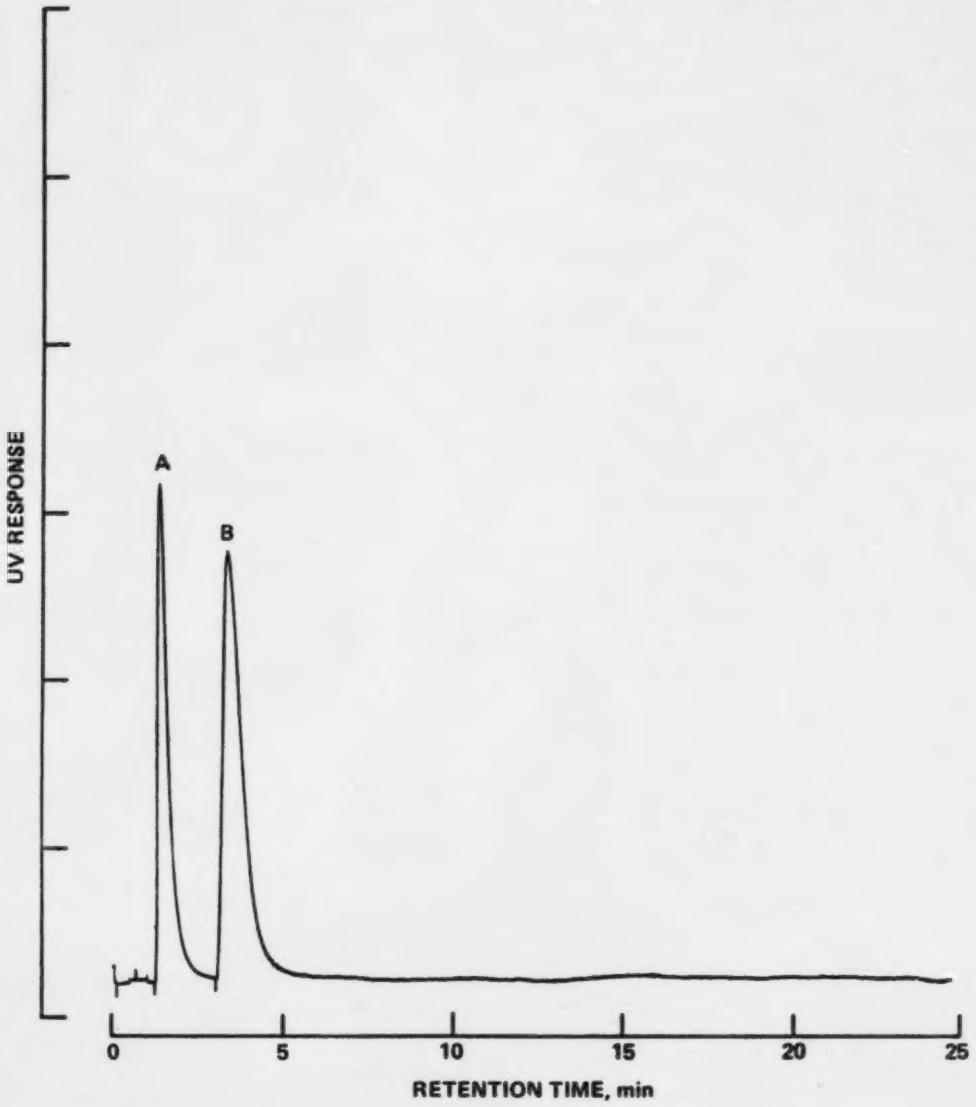


Figure C-1. Chromatogram by HPLC/UV (254 nm) for

(A) maleic anhydride(t_R = 1.5 min) and
(B) phthalic anhydride(t_R = 3.5 min).

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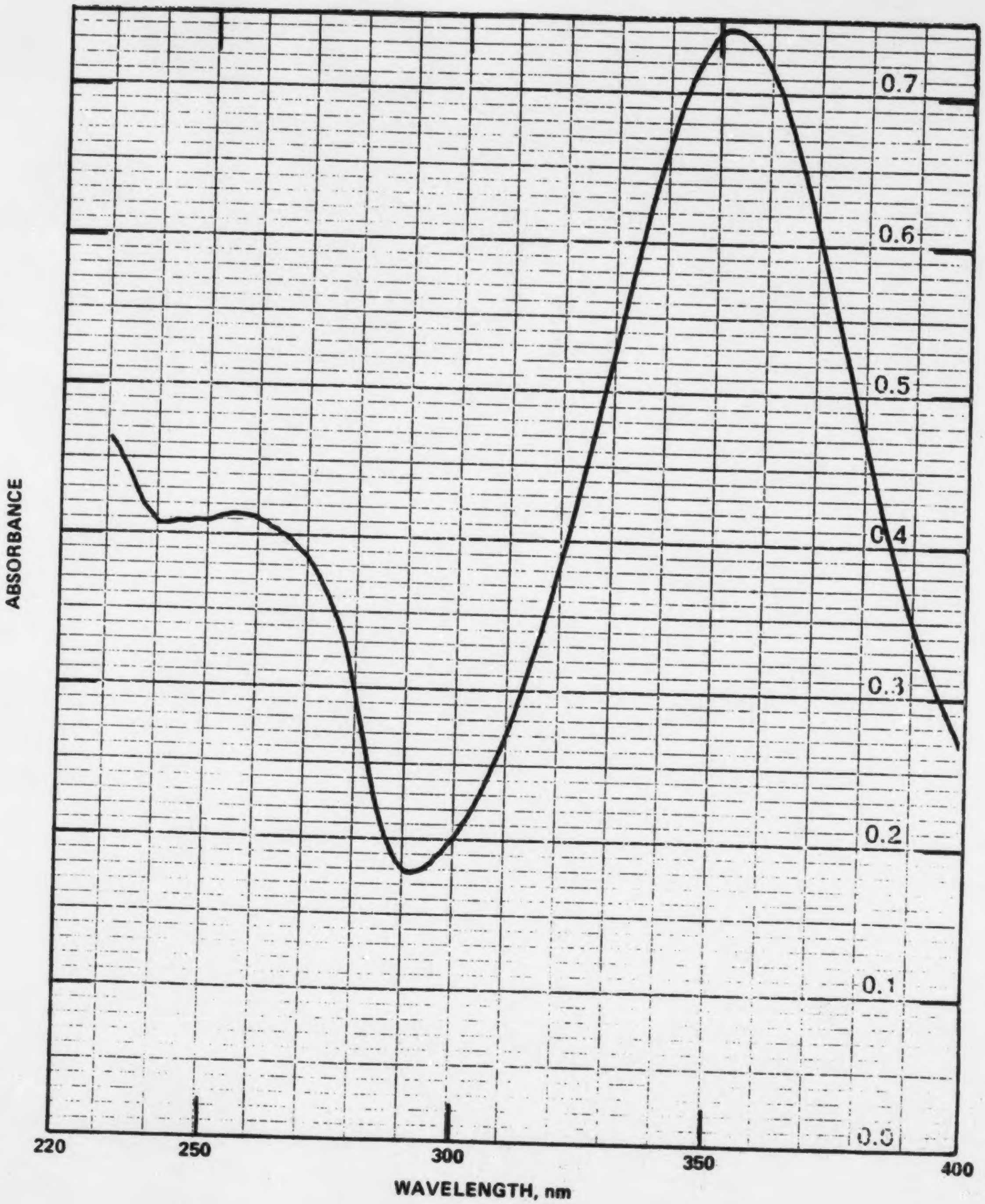

Figure C-2. UV spectrum for maleic anhydride.

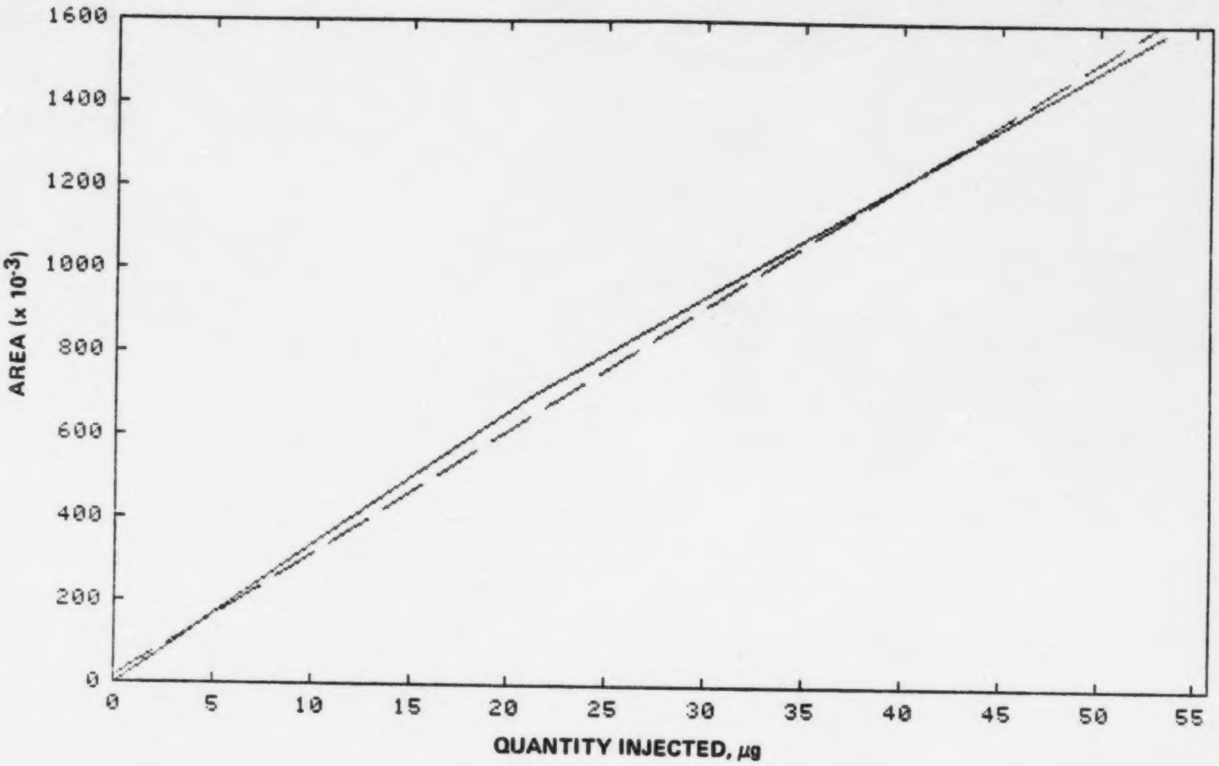

Figure C-3. Calibration curve for the determination of maleic anhydride by HPLC/UV (254 nm).

Range: 1.1 - 53 µg
Correlation coefficient: 0.999
Slope: 2.97×10^1
y-Intercept: 1.53×10^1

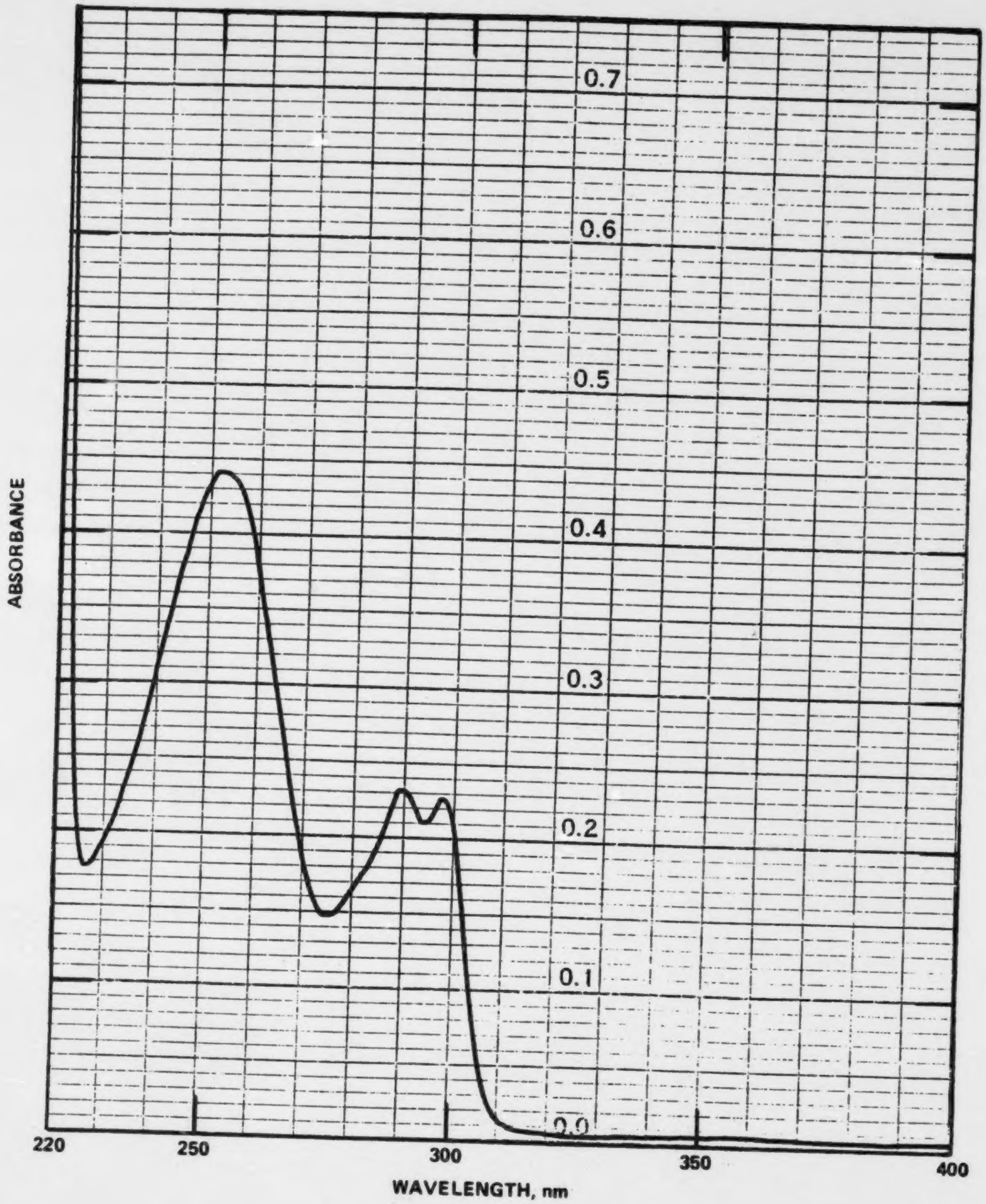

Figure C-4. UV spectrum for phthalic anhydride.

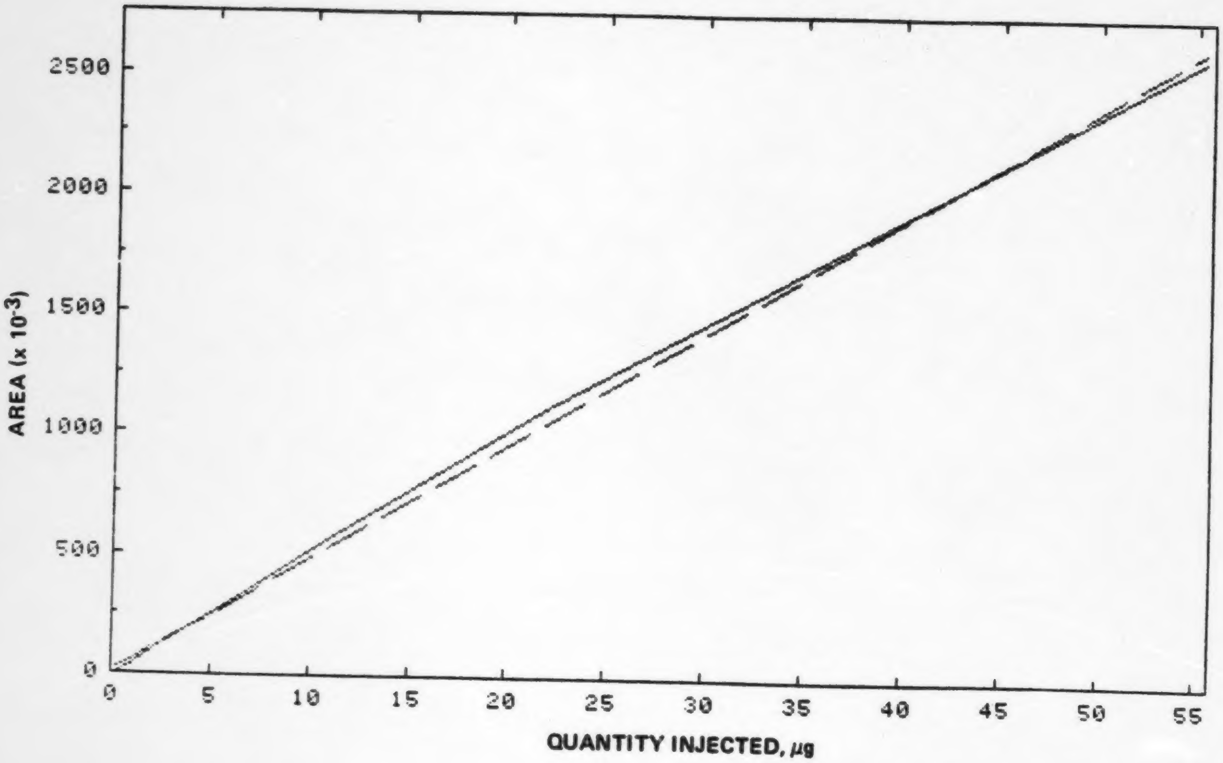

Figure C-5. Calibration curve for the determination of phthalic anhydride by HPLC/UV (254 nm).

Range: 1.1 - 55 µg
Correlation coefficient: 0.999
Slope: 4.71×10^1
y-Intercept: 1.41×10^1

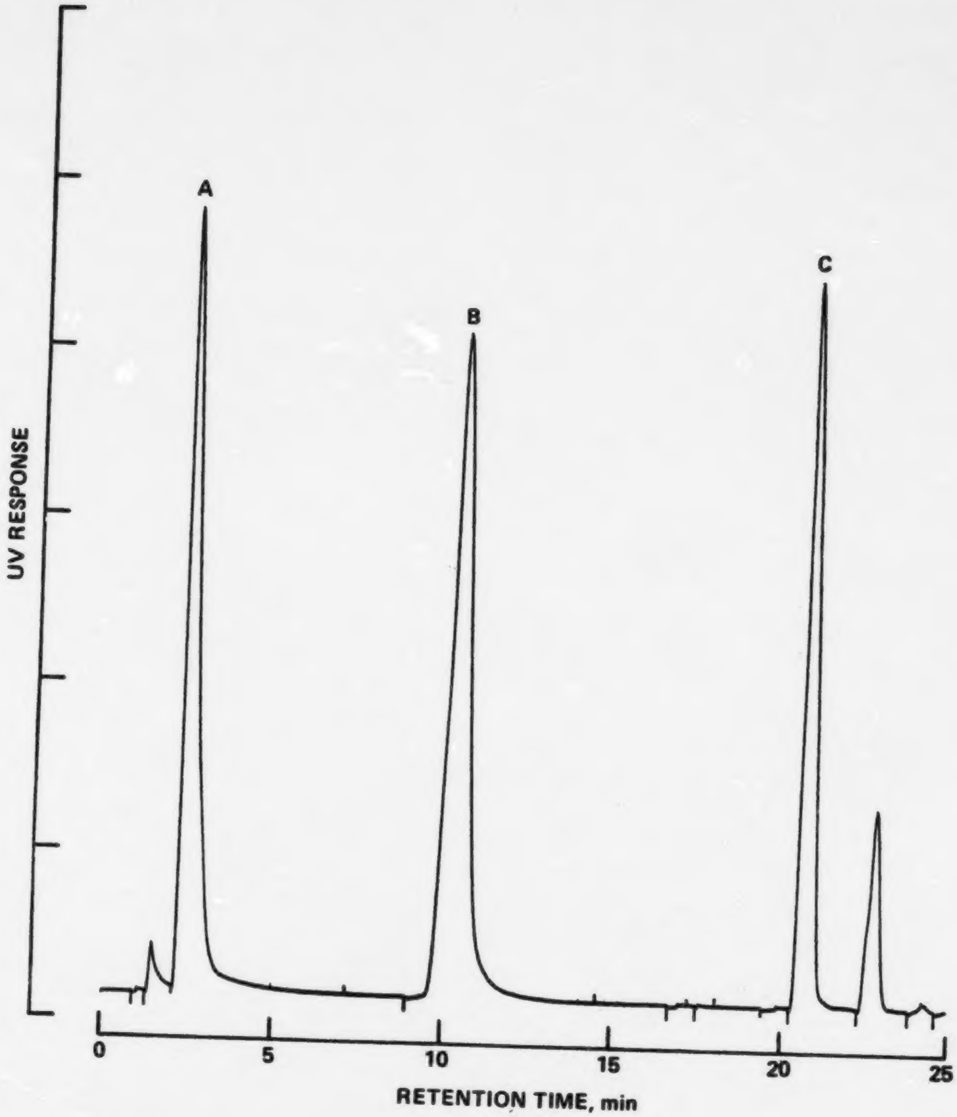

Figure C-6. Chromatogram by HPLC/UV for

(A) N-methyl-N'-nitro-N-nitrosoguanidine(t_R = 2.4 min),
(B) 4-nitroquinoline-1-oxide(t_R = 10.2 min), and
(C) diethylstilbestrol(t_R = 20.8 min).

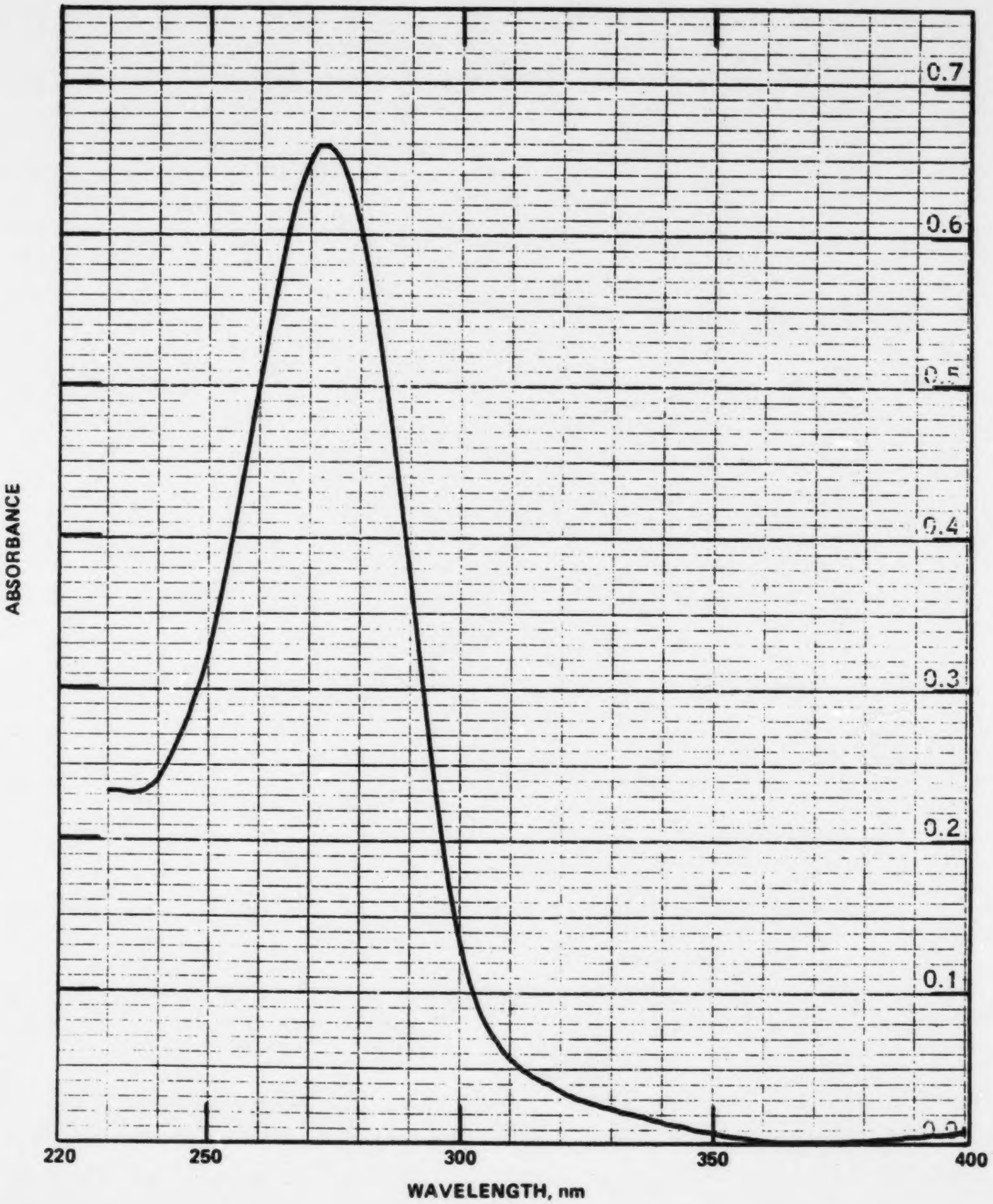

Figure C-7. UV spectrum for N-methyl-N'-nitro-N-nitrosoguanidine.

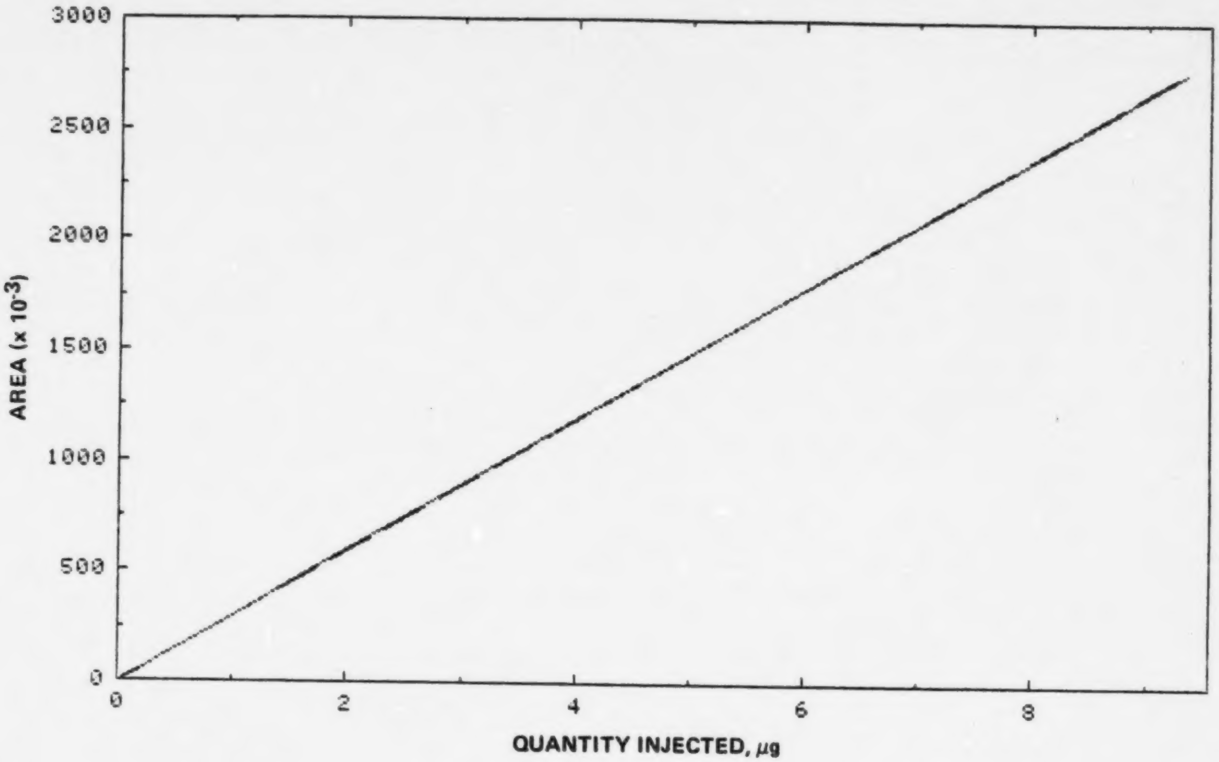

Figure C-8. Calibration curve for the determination of N-methyl-N'-nitro-N-nitrosoguanidine by HPLC/UV (254 nm).

Range: 0.037 - 9.4 µg
Correlation coefficient: 0.999
Slope: 2.97×10^2
y-Intercept: -2.56

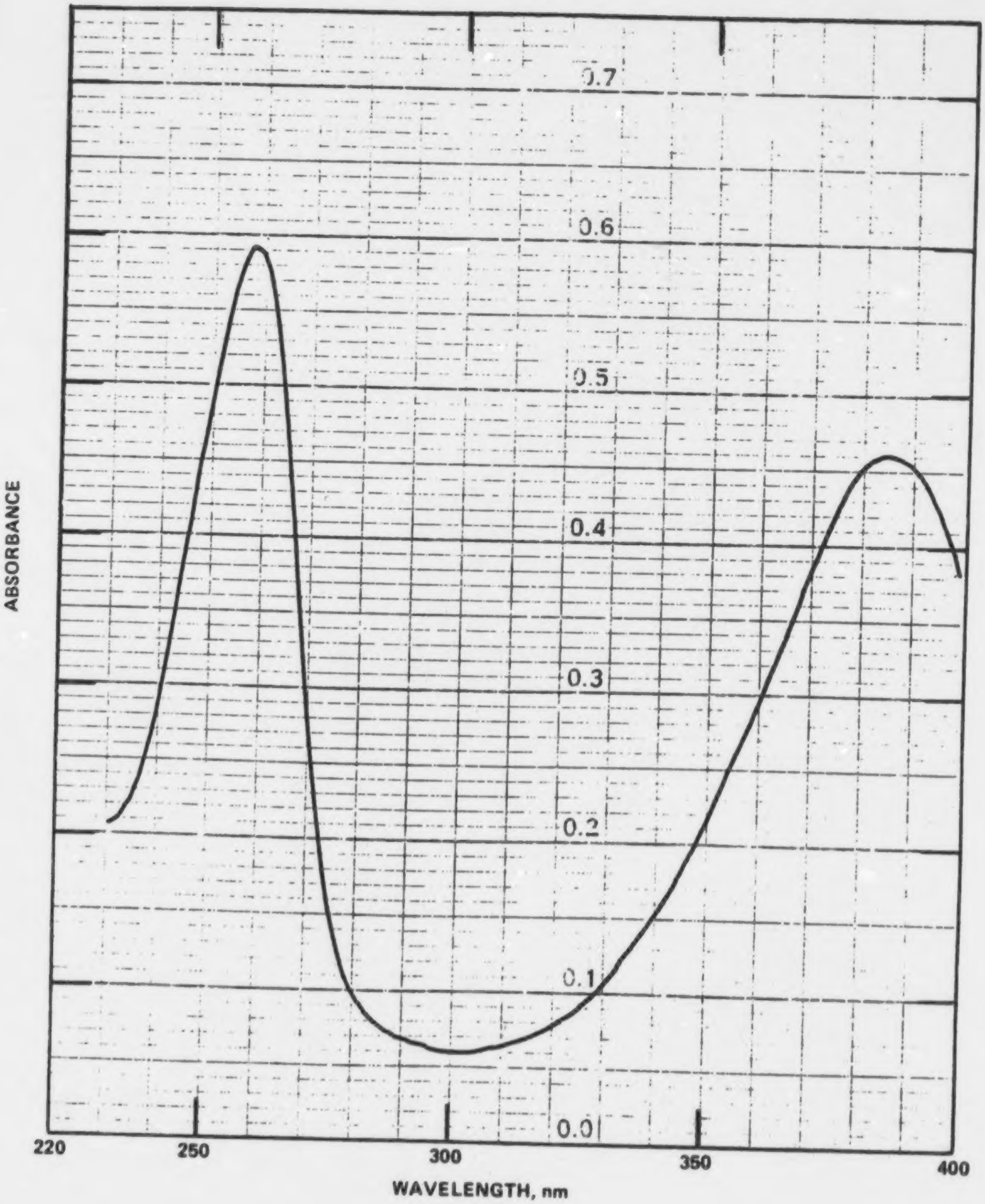

Figure C-9. UV spectrum for 4-nitroquinoline-1-oxide.

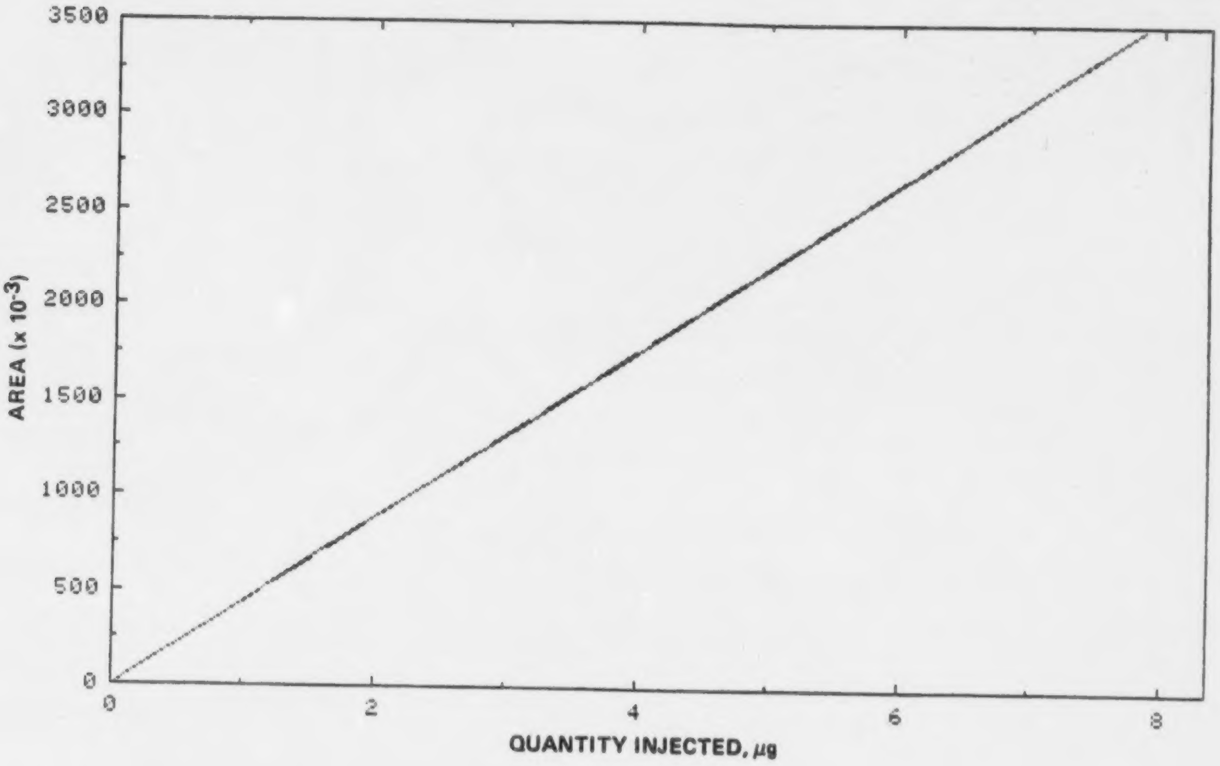

Figure C-10. Calibration curve for the determination of 4-nitroquinoline-1-oxide by HPLC/UV (254 nm)

Range: 0.031 - 7.8 µg
Correlation coefficient: 0.999
Slope: 4.43×10^2
y-Intercept: -1.90×10

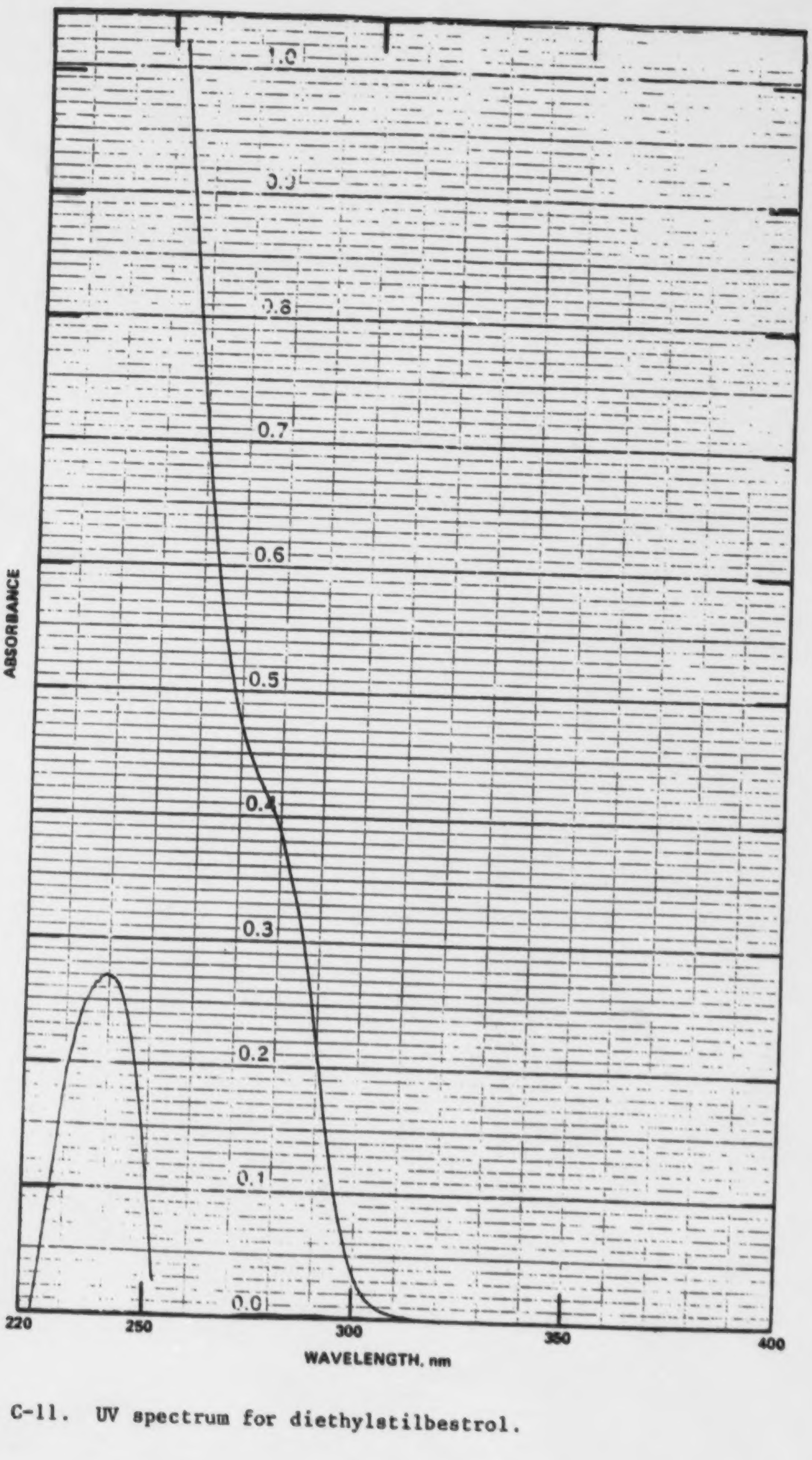

Figure C-11. UV spectrum for diethylstilbestrol.

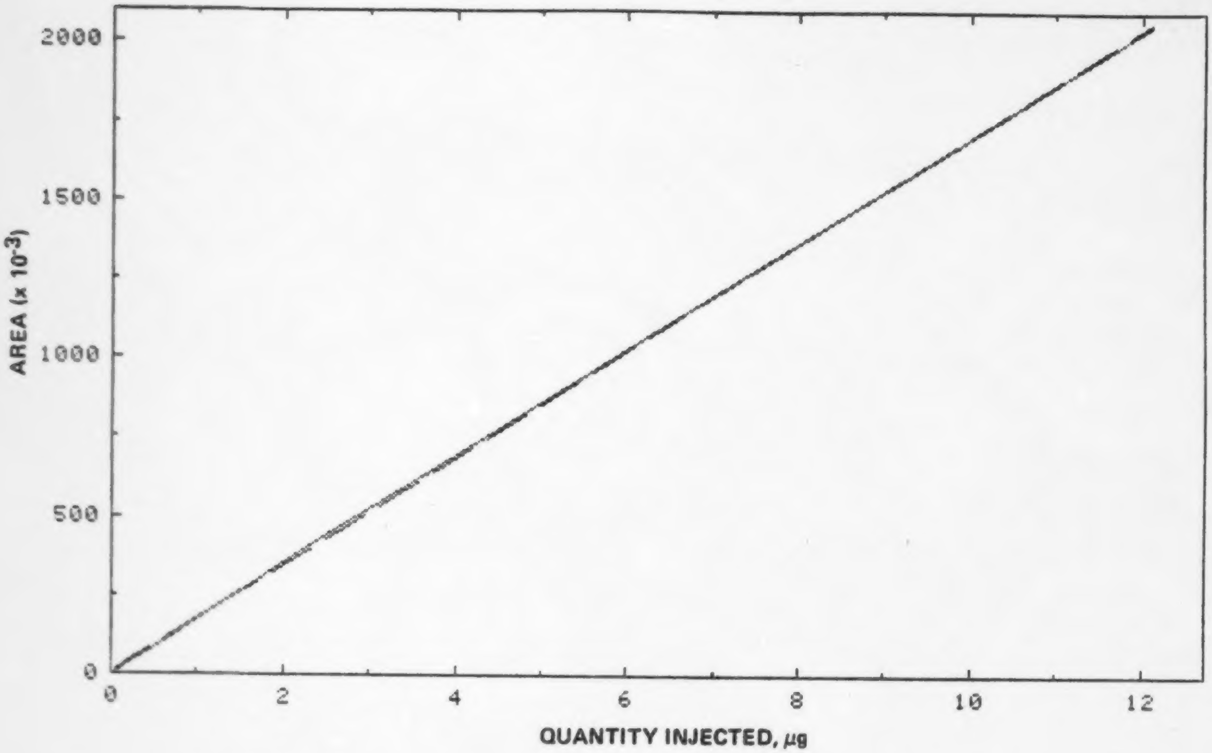

Figure C-12. Calibration curve for the determination of diethylstilbestrol by HPLC/UV (254 nm).

Range: 0.12 - 12 µg
Correlation coefficient: 0.999
Slope: 1.70×10^2
y-Intercept: 4.87×10

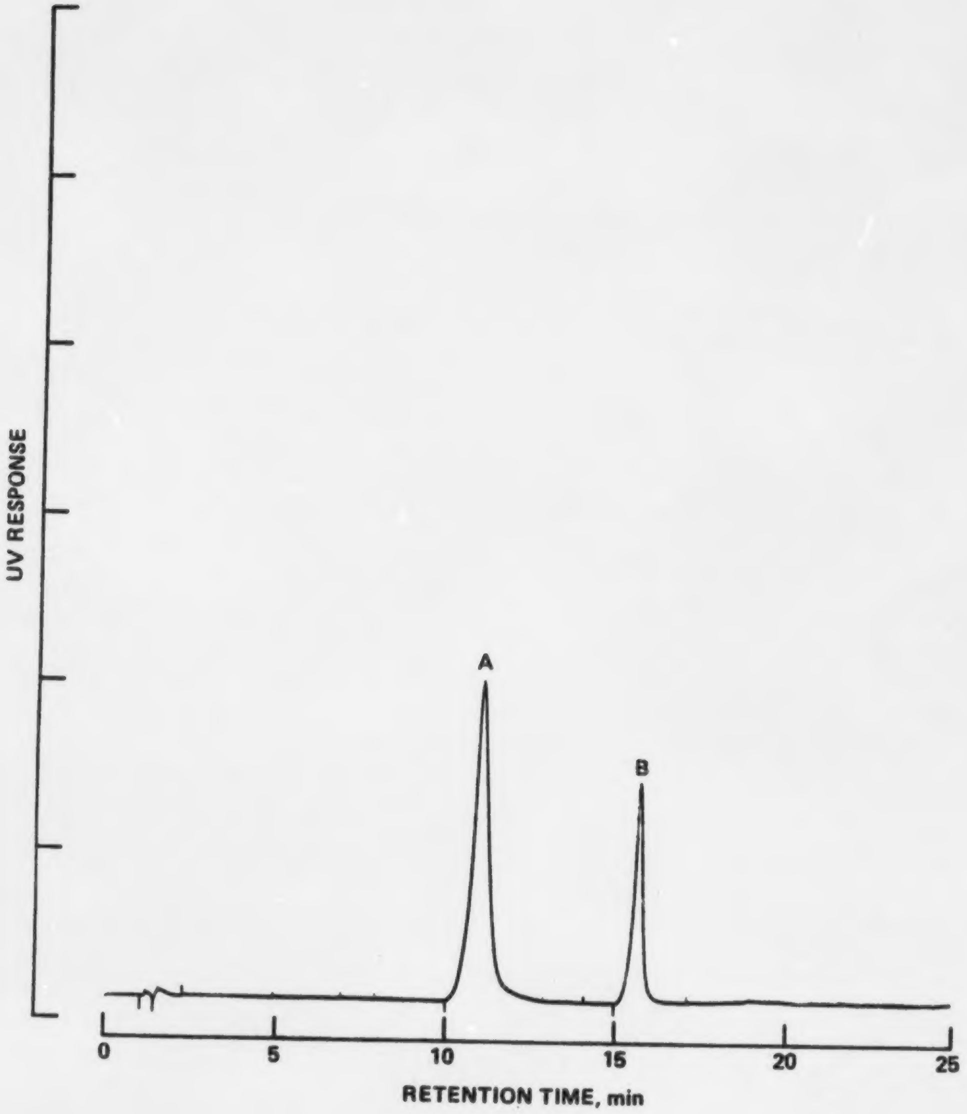

Figure C-13. Chromatogram by HPLC/UV (254 nm) for

(A) 3-methylphenol(t_R = 11.1 min) and
(B) 2,6-dichlorophenol(t_R = 15.8 min).

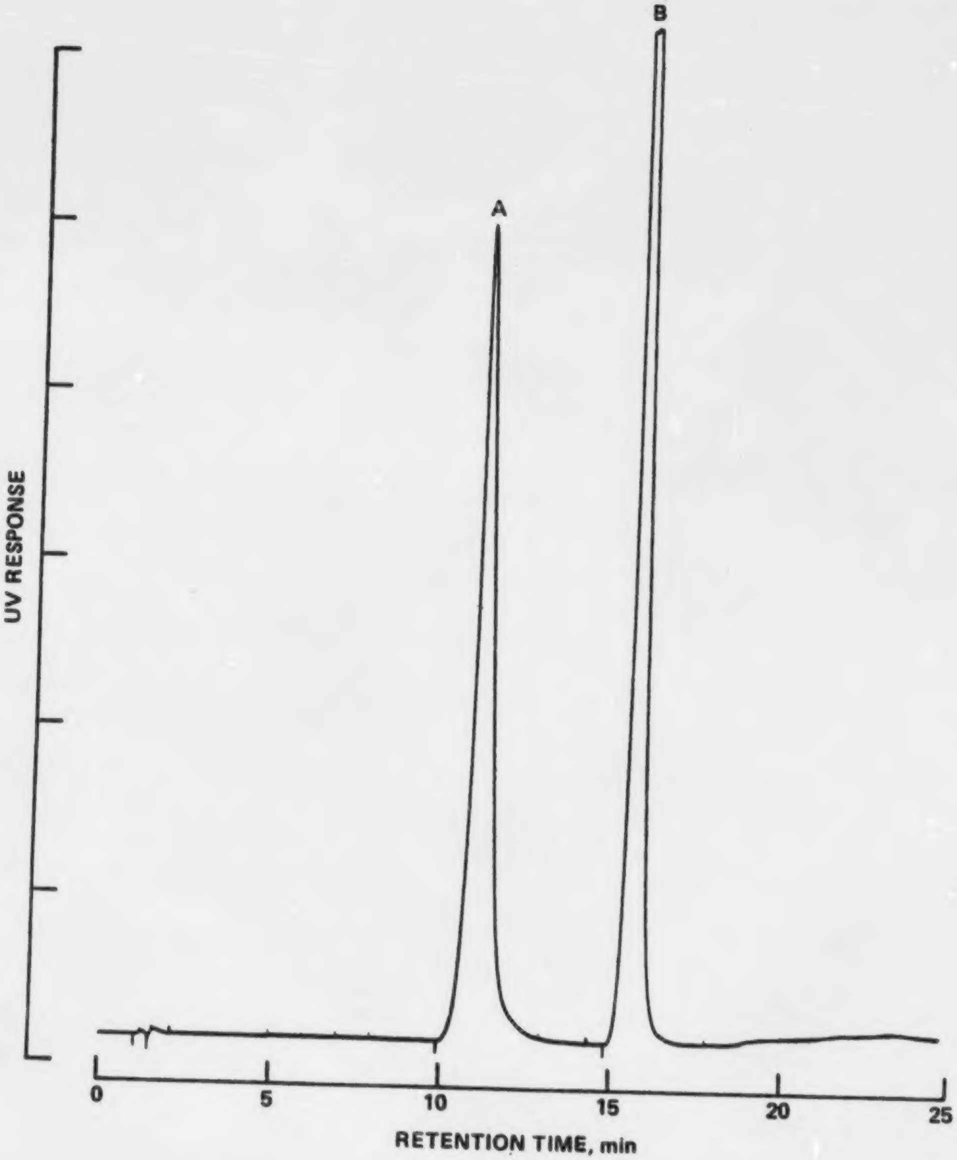

Figure C-14. Chromatogram by HPLC/UV (280 nm) for

(A) 3-methylphenol(t_R = 11.1 min) and
(B) 2,6-dichlorophenol(t_R = 15.8 min).

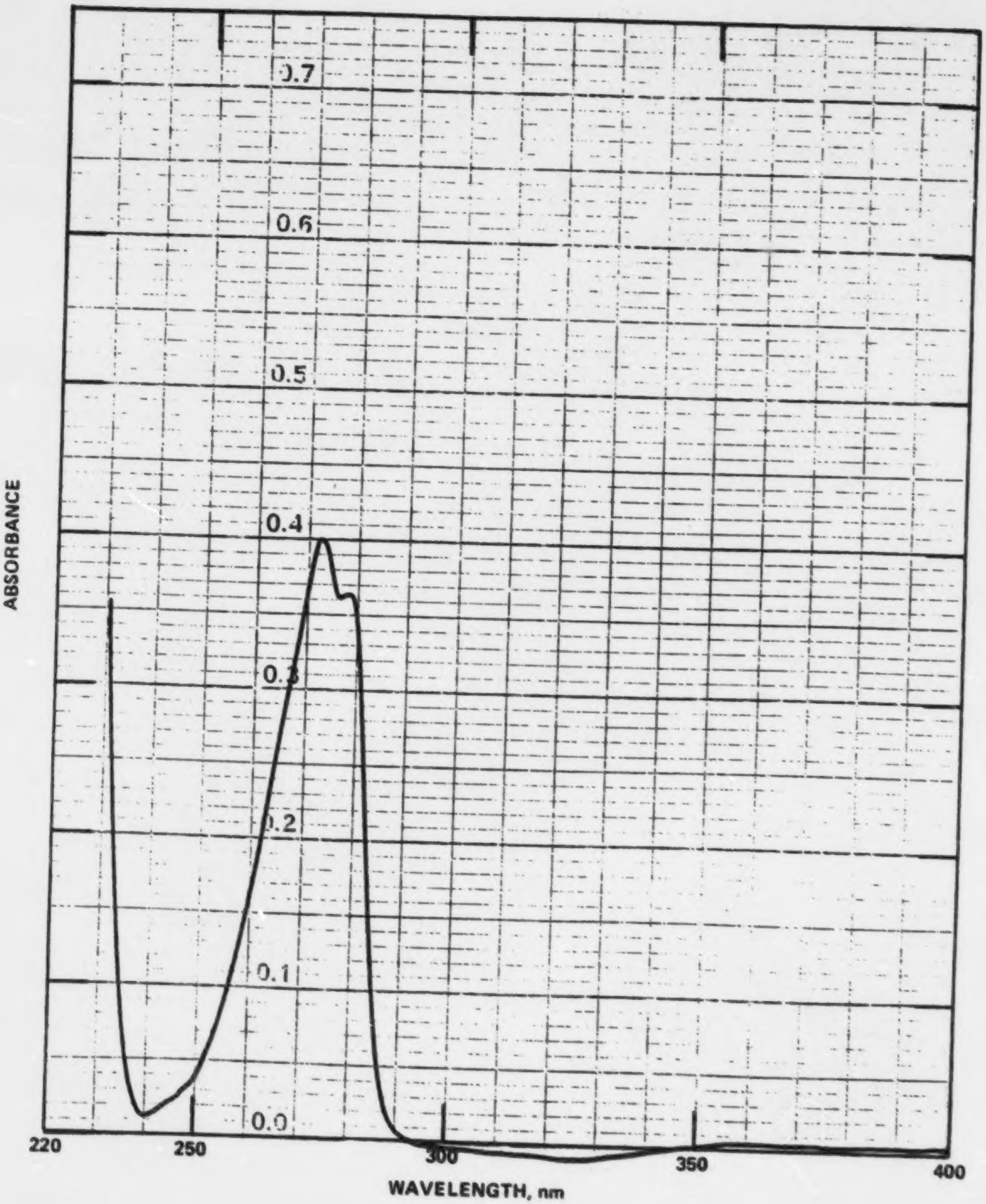

Figure C-15. UV spectrum for 3-methylphenol.

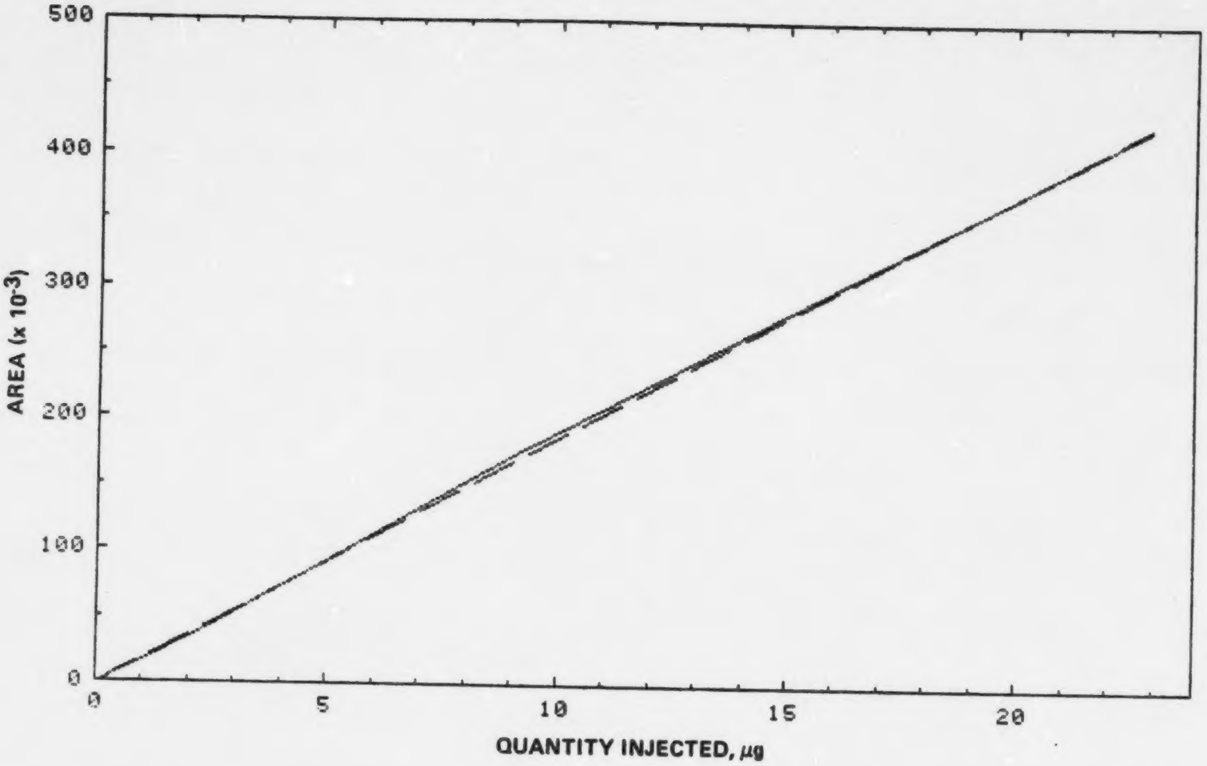

Figure C-16. Calibration curve for the determination of 3-methylphenol by HPLC/UV (254 nm).

Range: 0.092 - 23 µg
Correlation coefficient: 0.999
Slope: 1.86×10^1
y-Intercept: -1.23

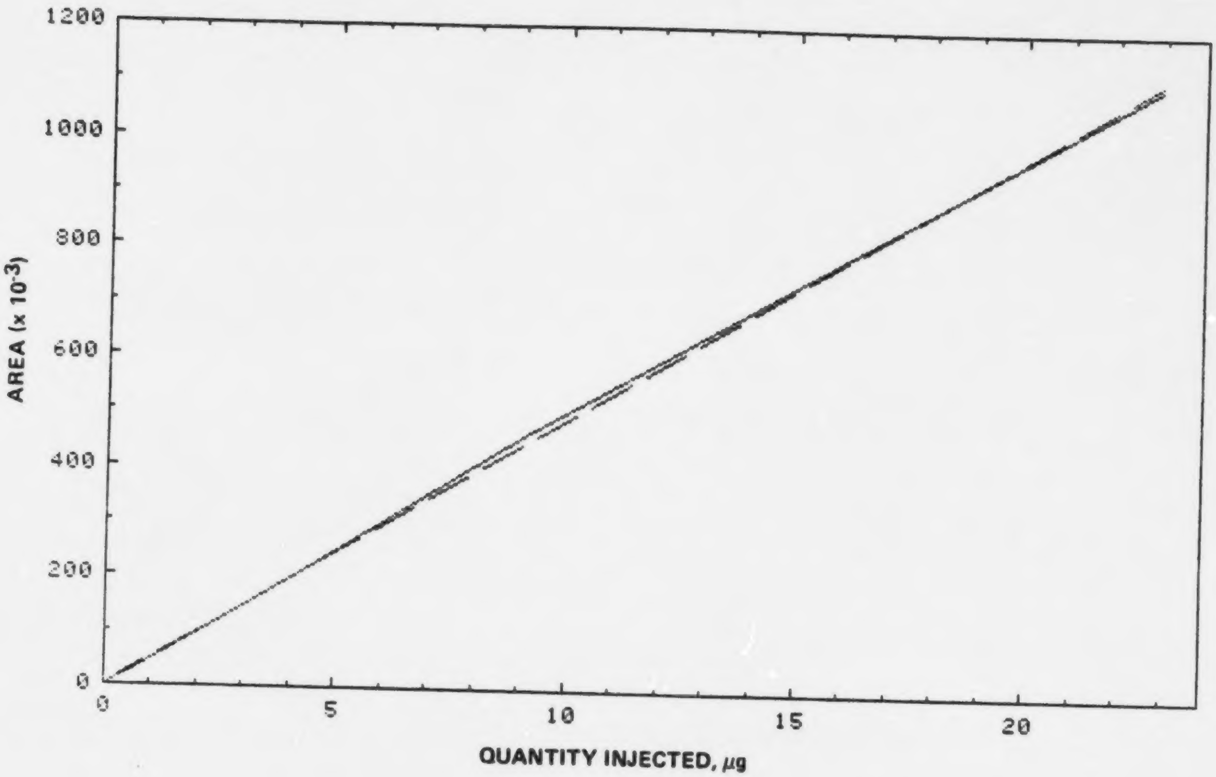

Figure C-17. Calibration curve for the determination of 3-methylphenol by HPLC/UV (280 nm).

Range: 0.23 - 23 μg
Correlation coefficient: 0.999
Slope: 4.85×10^1
y-Intercept: 1.39

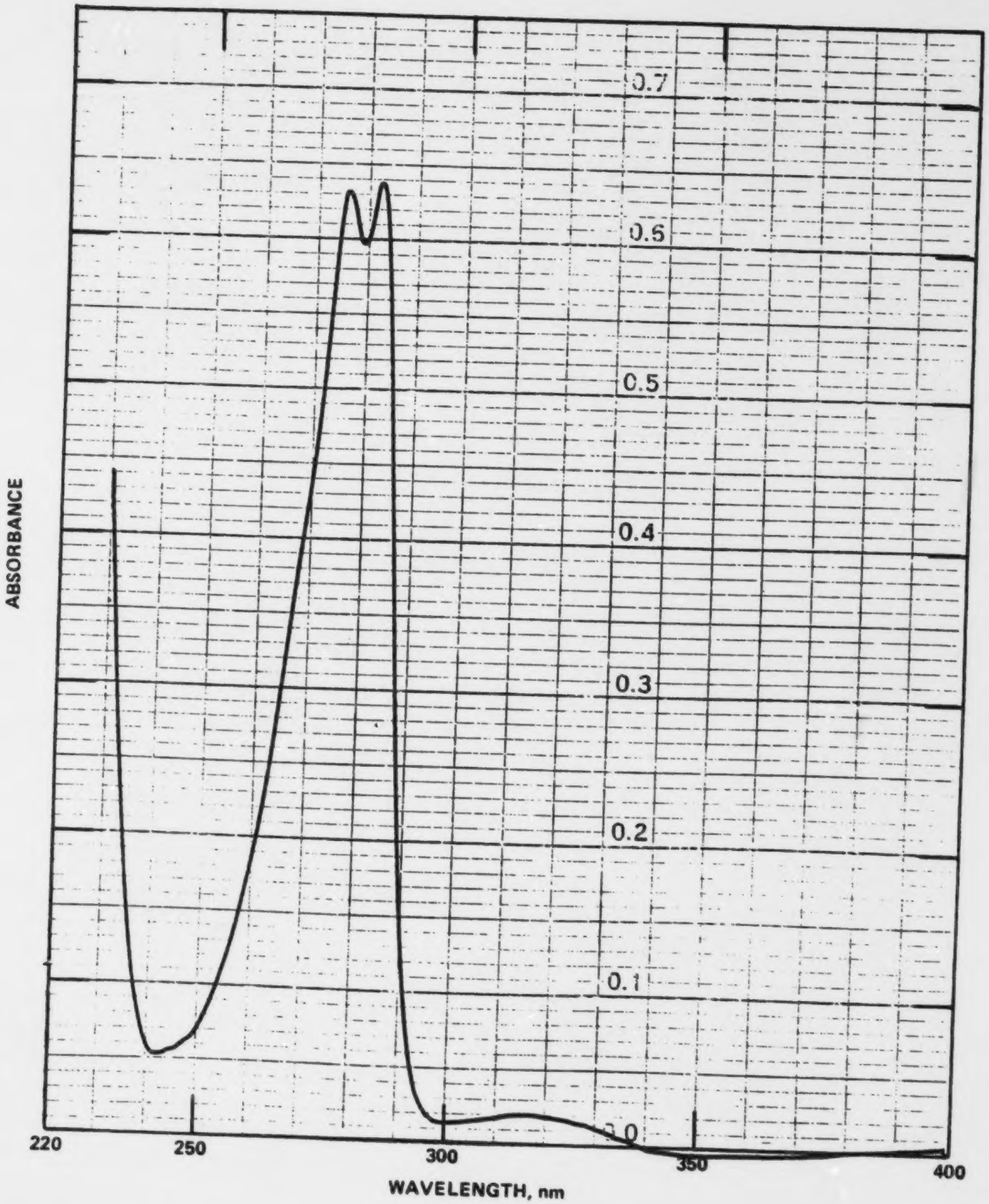

Figure C-18. UV spectrum for 2,6-dichlorophenol.

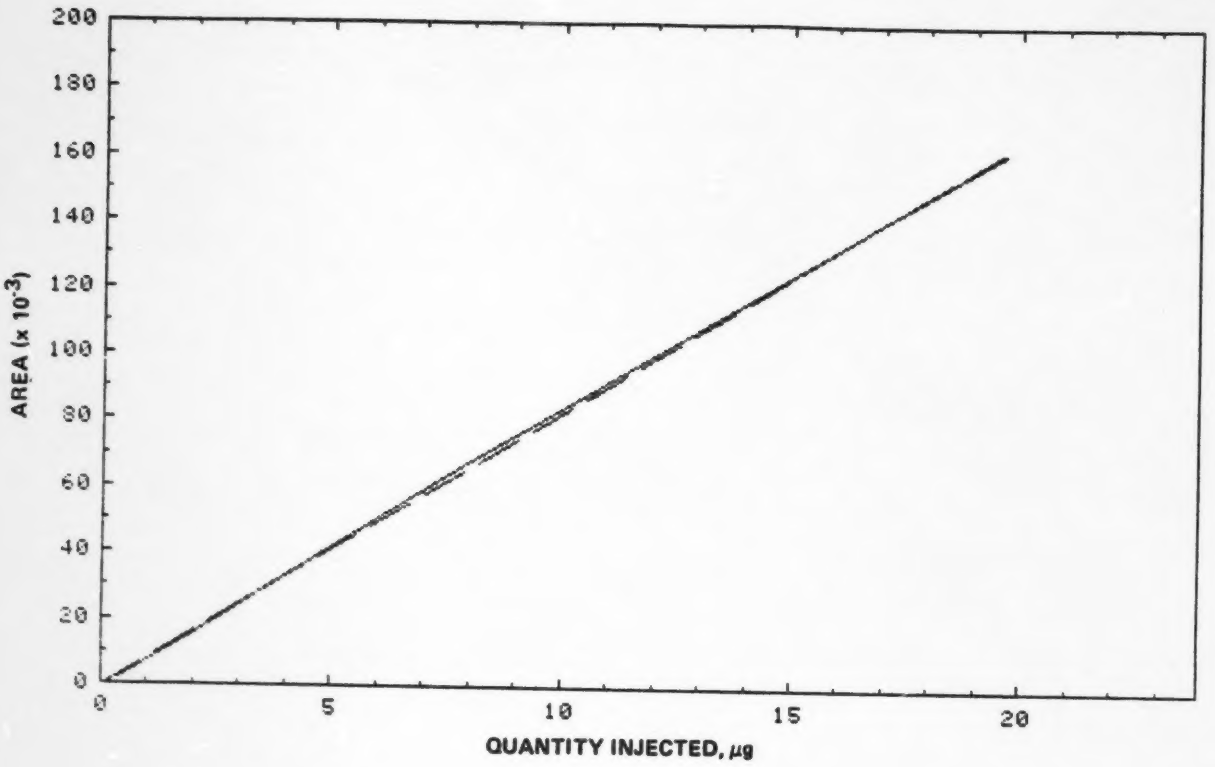

Figure C-19. Calibration curve for the determination of 2,6-dichlorophenol by HPLC/UV (254 nm).

Range: 0.20 - 20 µg
Correlation coefficient: 0.999
Slope: 8.31
y-Intercept: -6.73×10^{-1}

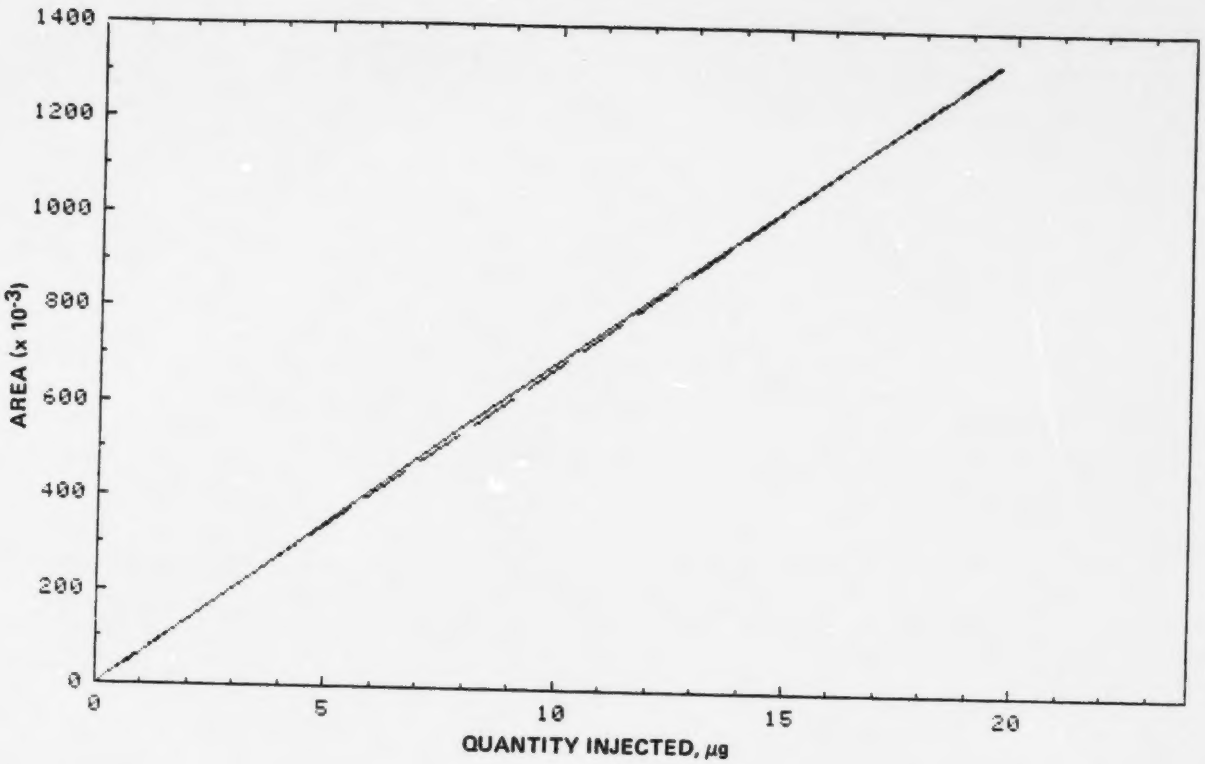

Figure C-20. Calibration curve for the determination of 2,6-dichlorophenol by HPLC/UV (280 nm).

Range: 0.20 - 20 μg
Correlation coefficient: 0.999
Slope: 6.81×10^{1}
y-Intercept: 6.47×10^{-1}

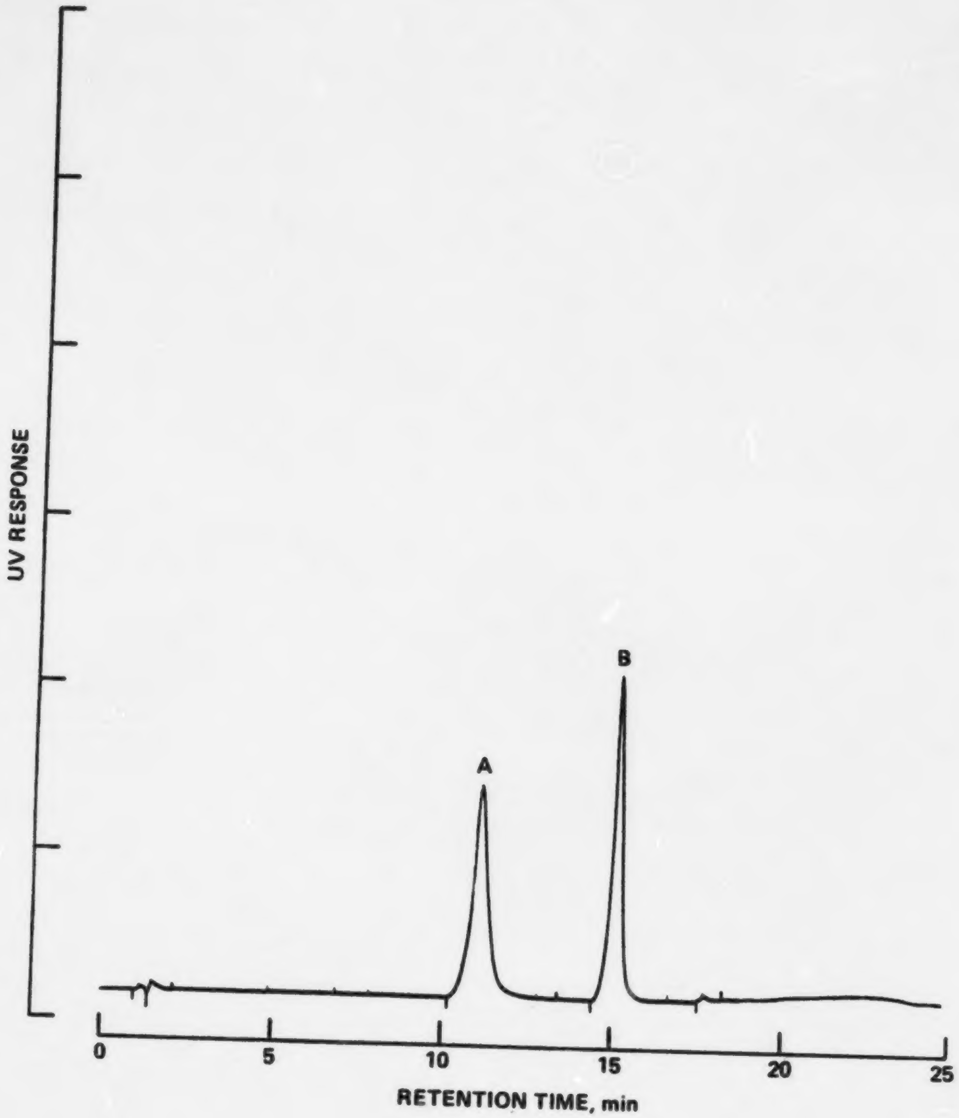

Figure C-21. Chromatogram by HPLC/UV (254 nm) for

(A) 4-methylphenol(t_R = 11.2 min) and
(B) 2,4-dimethylphenol(t_R = 15.3 min).

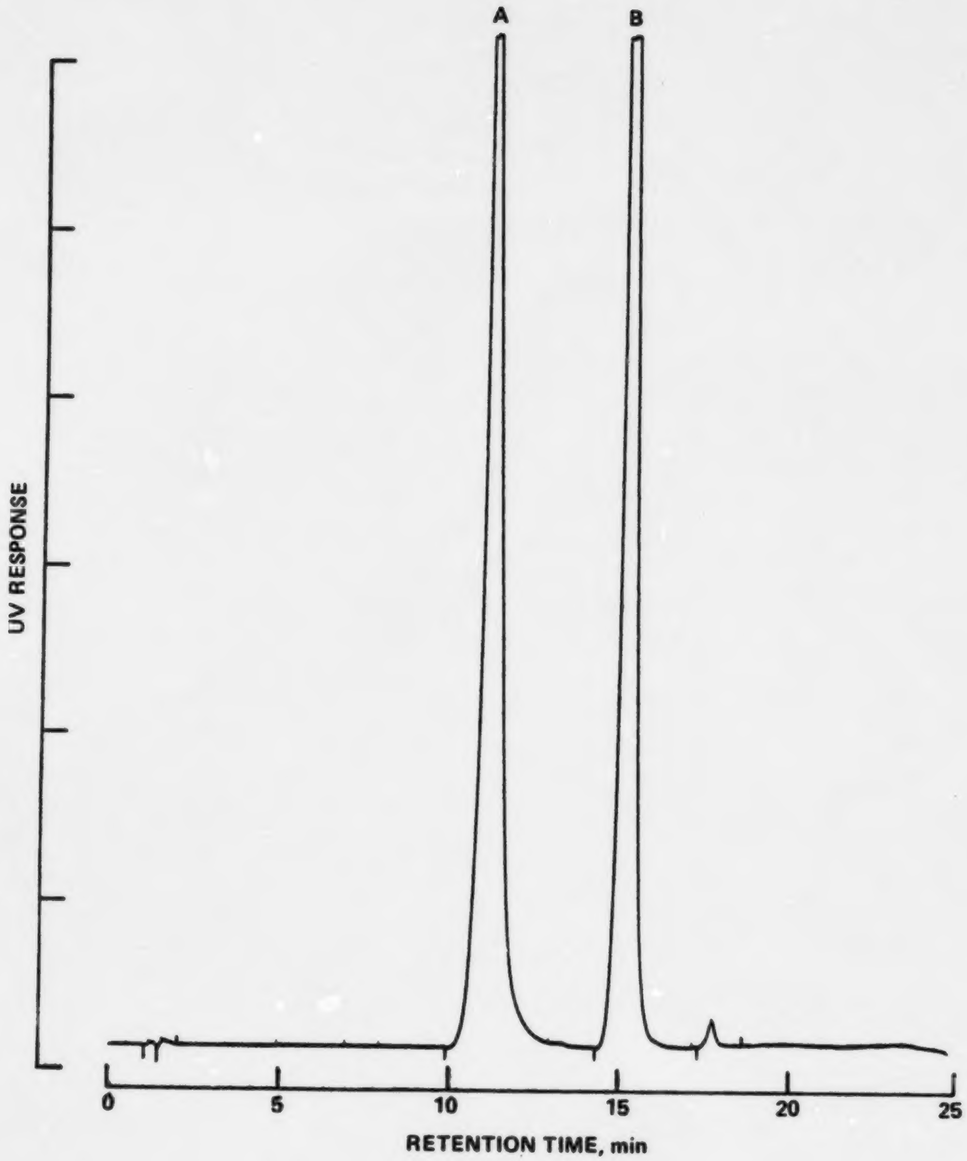

Figure C-22. Chromatogram by HPLC/UV (280 nm) for

(A) 4-methylphenol(t_R = 11.2 min) and
(B) 2,4-dimethylphenol(t_R = 15.3 min).

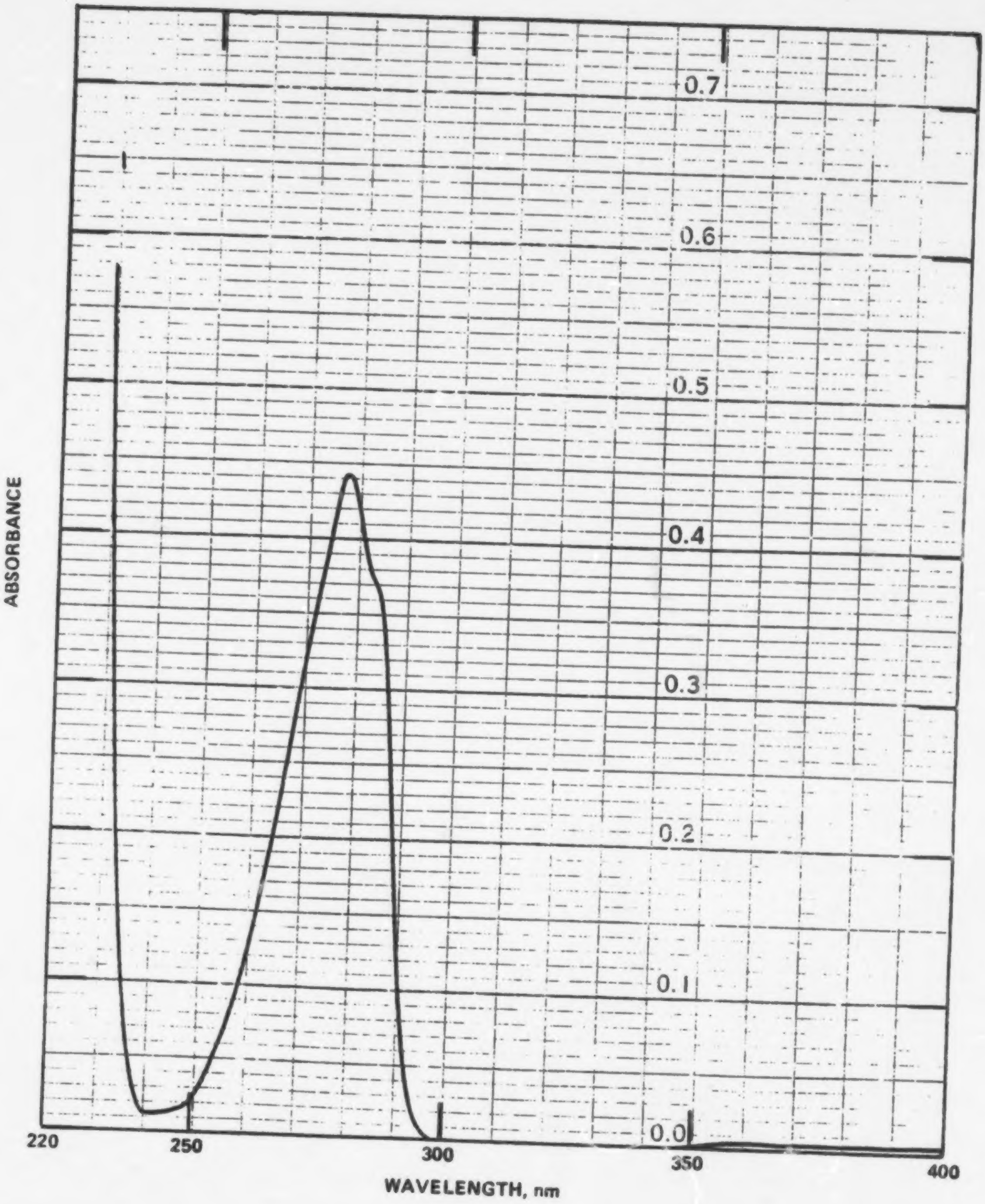

Figure C-23. UV spectrum for 4-methylphenol.

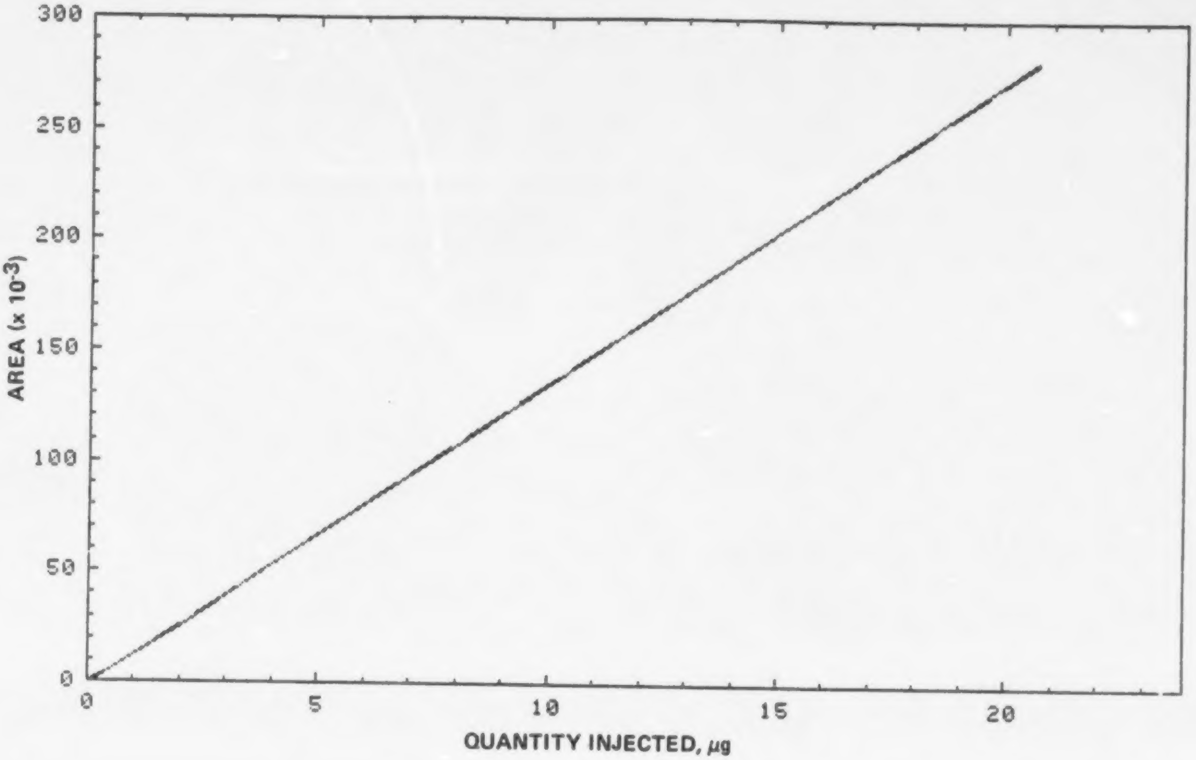

Figure C-24. Calibration curve for the determination of 4-methylphenol by HPLC/UV (254 nm).

Range: 0.41 - 21 μg
Correlation coefficient: 0.999
Slope: 1.37×10^1
y-Intercept: -1.50

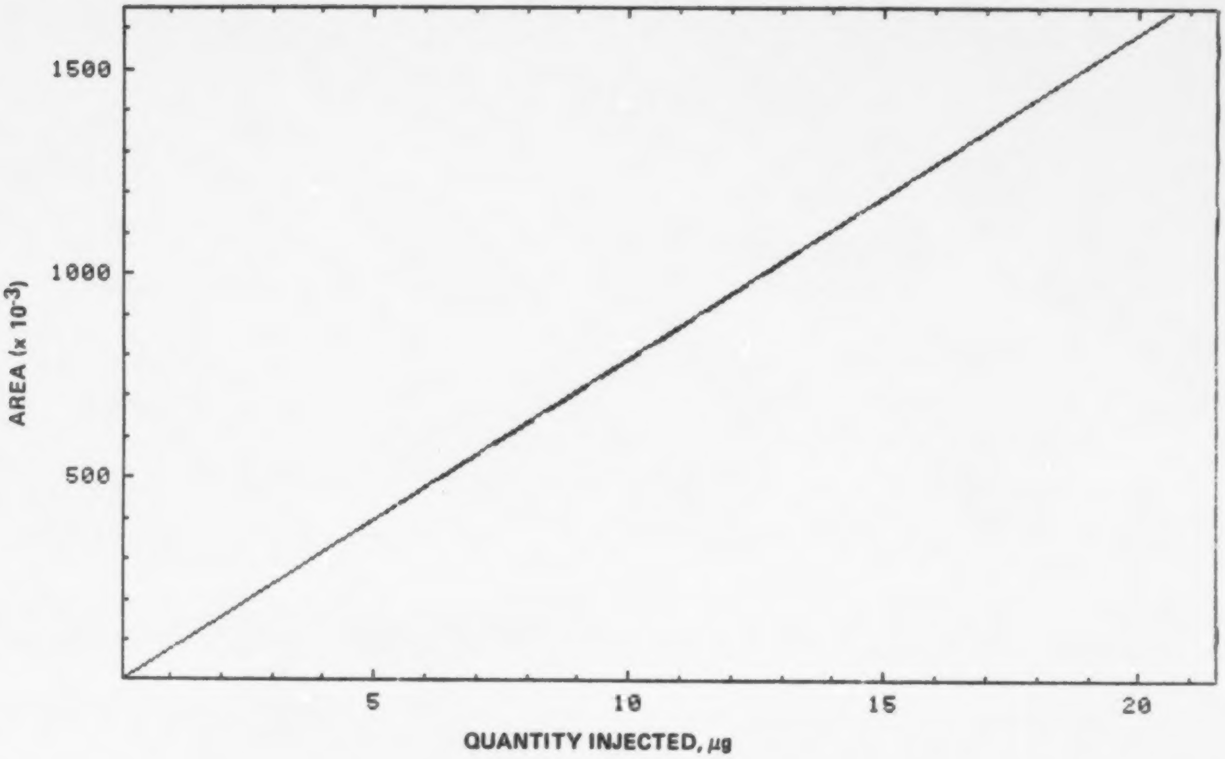

Figure C-25. Calibration curve for the determination of 4-methylphenol by HPLC/UV (280 nm).

Range: 0.21 - 21 μg
Correlation coefficient: 0.999
Slope: 7.95×10^1
y-Intercept: -1.56

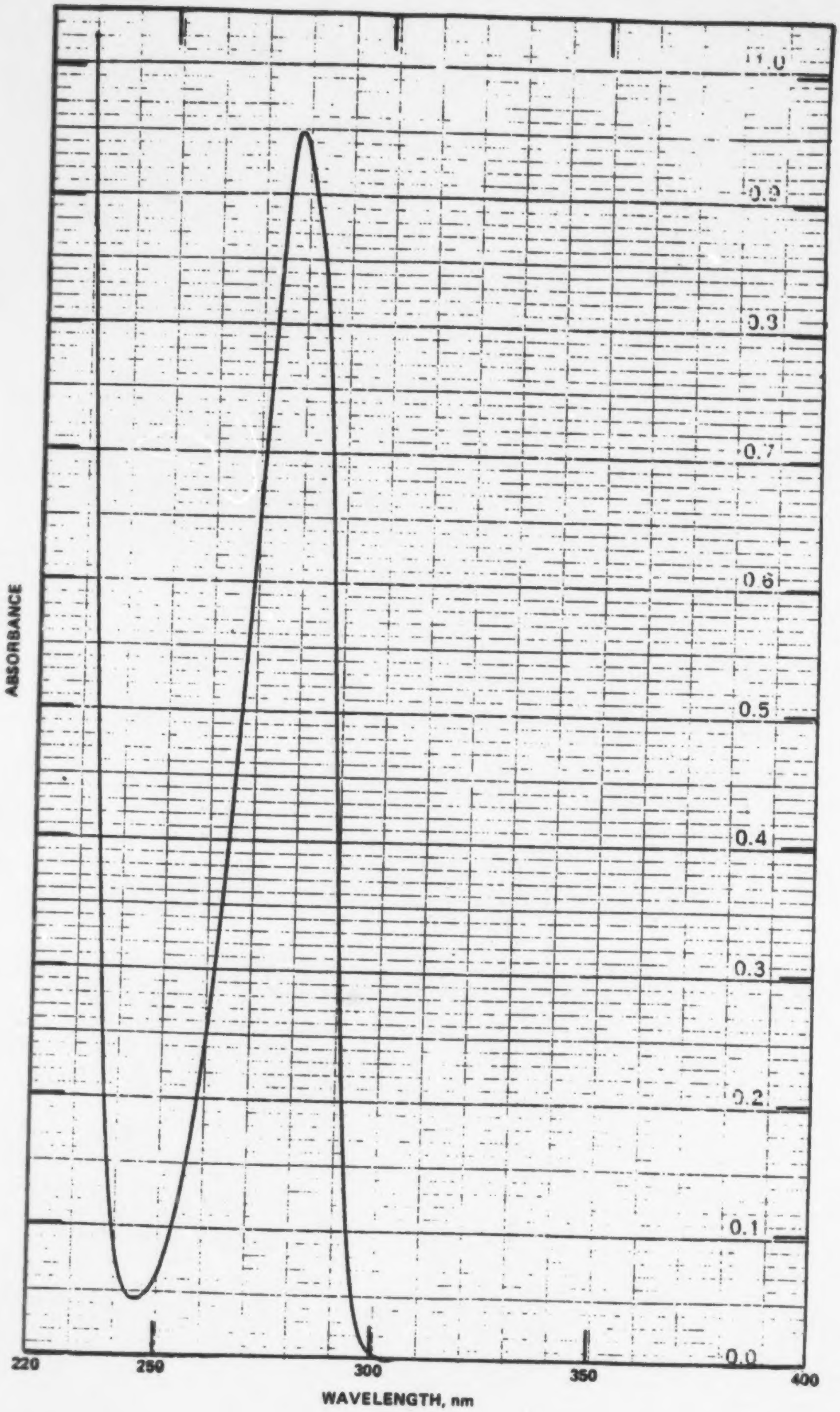

Figure C-26. UV spectrum for 2,4-dimethylphenol.

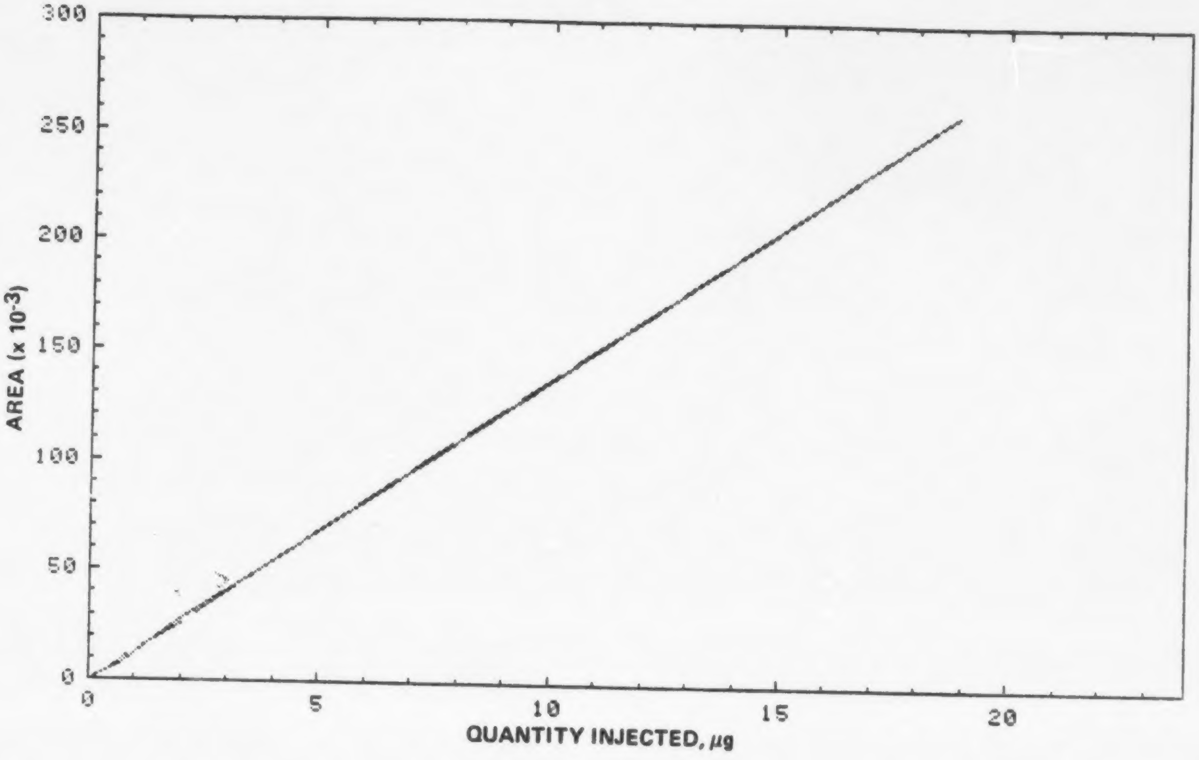

Figure C-27. Calibration curve for the determination of 2,4-dimethylphenol by HPLC/UV (254 nm).

Range: 0.19 - 19 µg
Correlation coefficient: 0.999
Slope: 1.38×10^{1}
y-Intercept: -9.63×10^{-1}

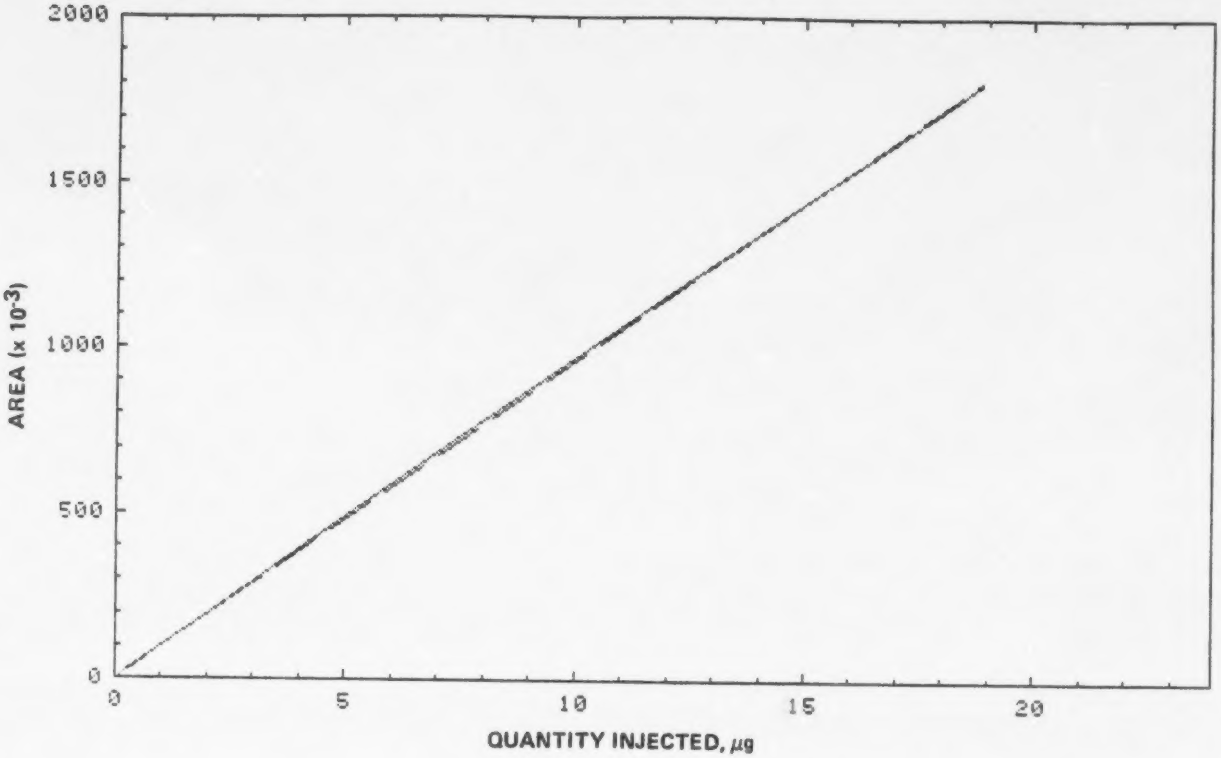

Figure C-28. Calibration curve for the determination of 2,4-dimethylphenol by HPLC/UV (280 nm).

Range: 0.19 - 19 µg
Correlation coefficient: 0.999
Slope: 9.58×10^1
y-Intercept: 2.21

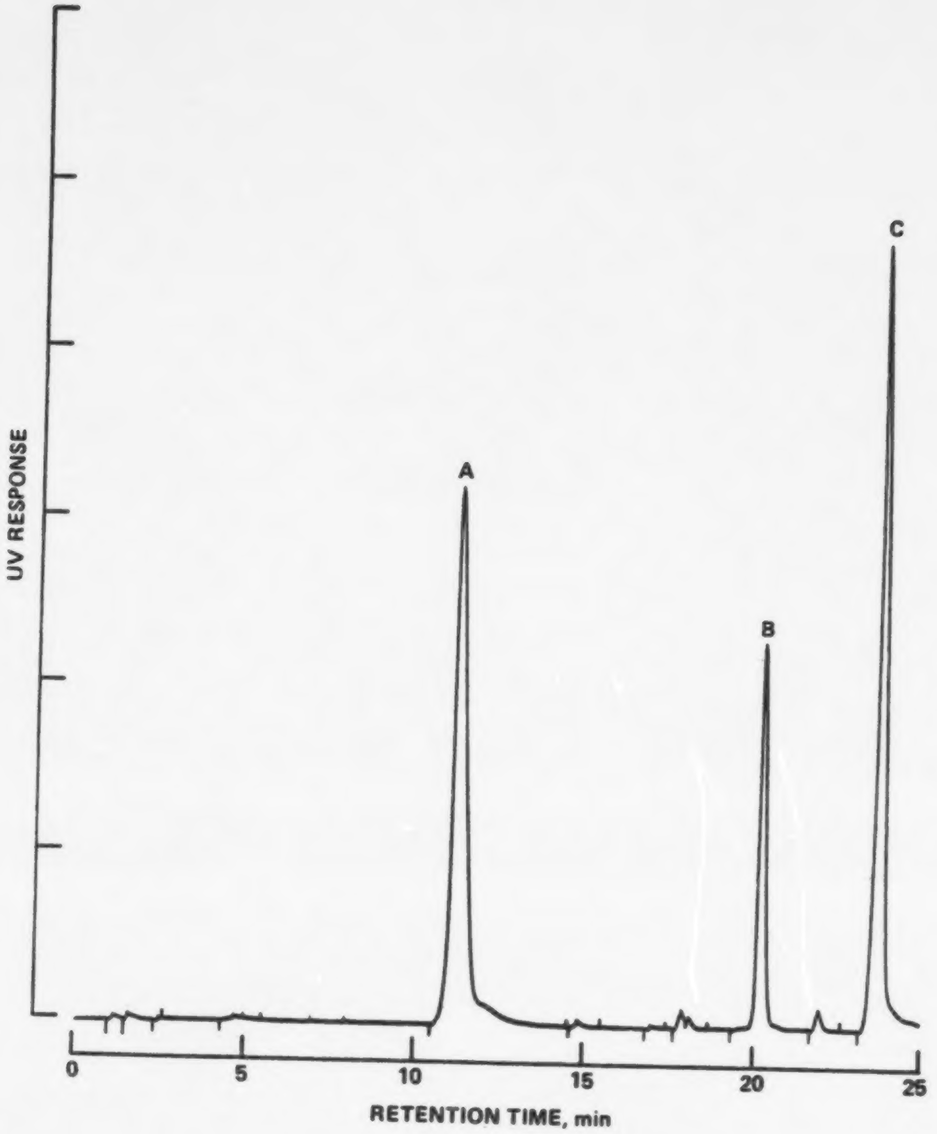

Figure C-29. Chromatogram by HPLC/UV (254 nm) for

(A) 2-methylphenol(t_R = 11.3 min),
(B) 2,4,5-trichlorophenol(t_R = 20.3 min), and
(C) pentachlorophenol(t_R = 23.8 min).

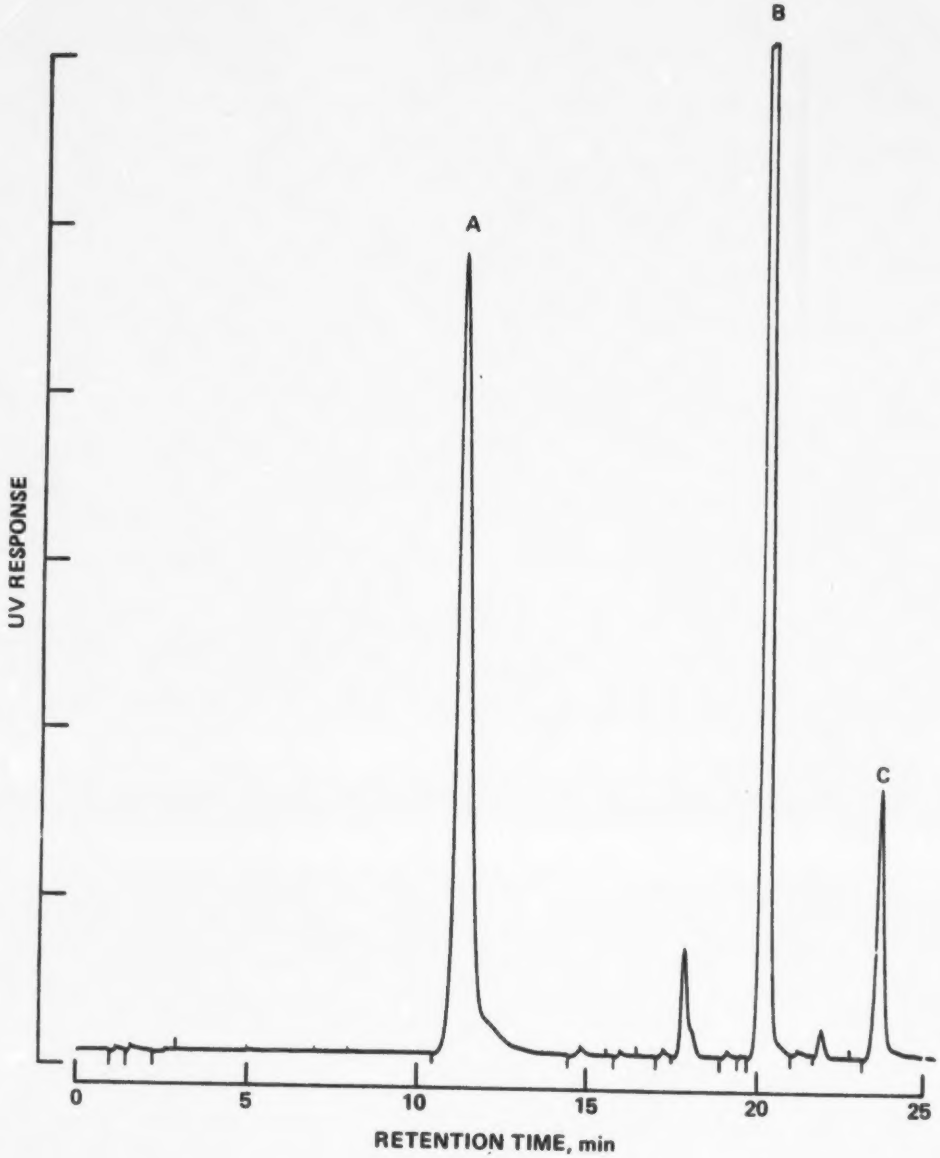

Figure C-30. Chromatogram by HPLC/UV (280 nm) for

(A) 2-methylphenol(t_R = 11.3 min),
(B) 2,4,5-trichlorophenol(t_R = 20.3 min), and
(C) pentachlorophenol(t_R = 23.8 min).

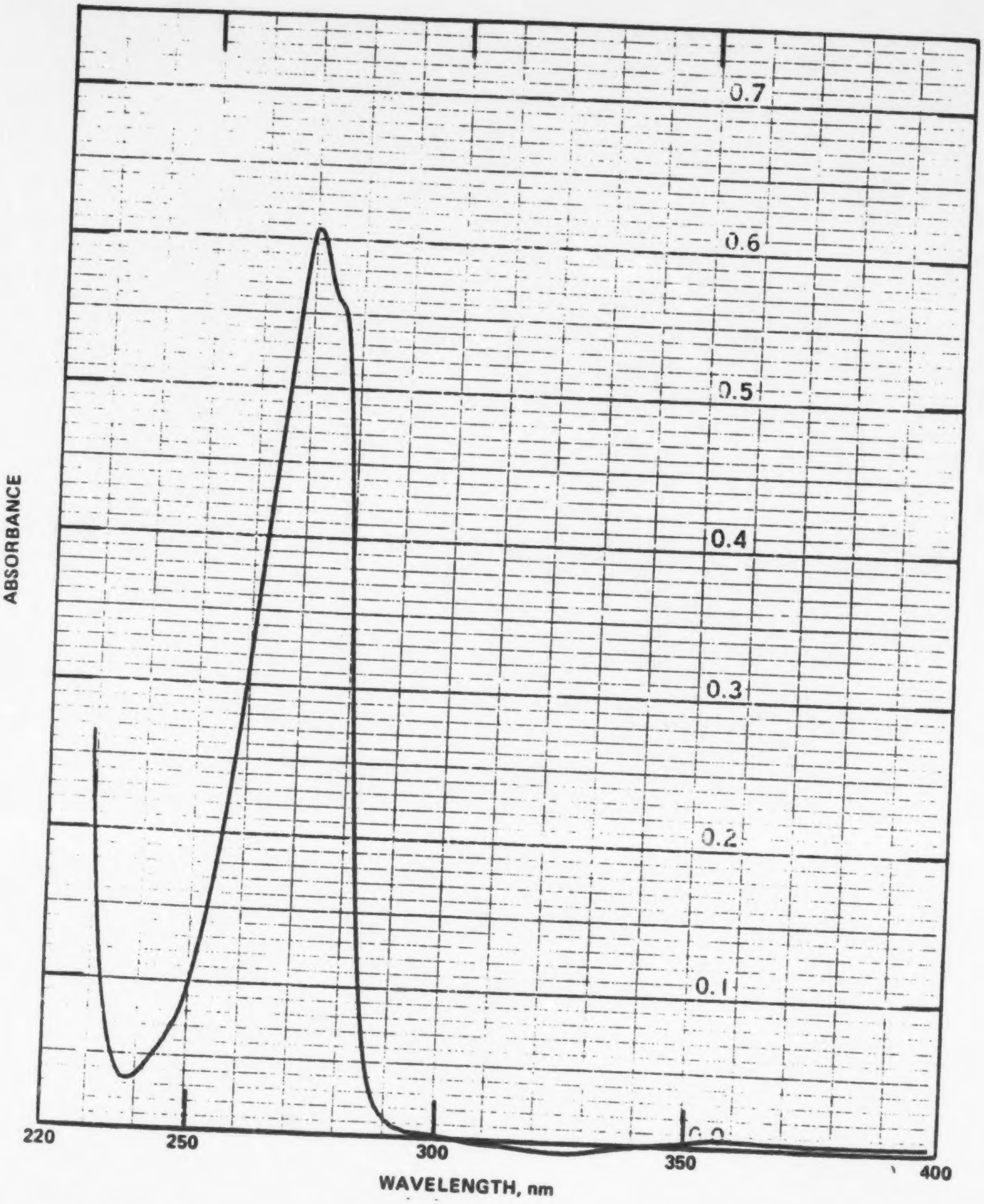

Figure C-31. UV spectrum for 2-methylphenol.

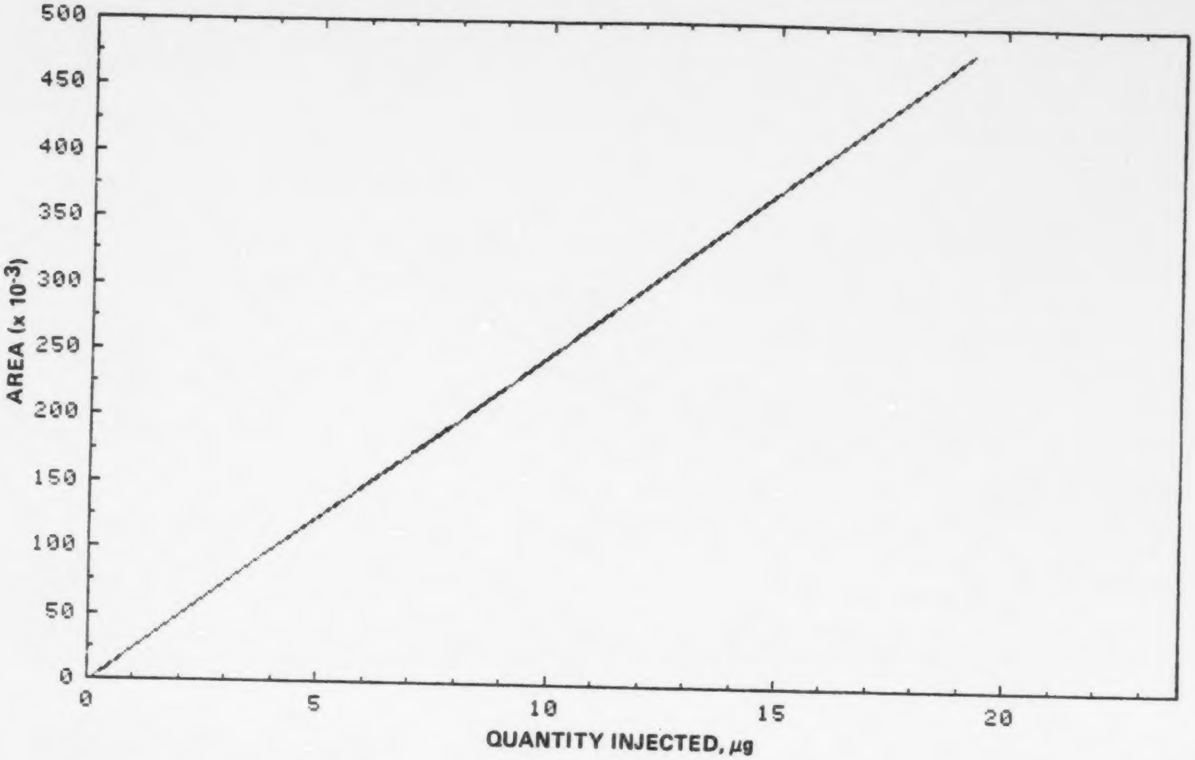

Figure C-32. Calibration curve for the determination of 2-methylphenol by HPLC/UV (254 nm).

Range: 0.20 - 19 µg
Correlation coefficient: 0.999
Slope: 2.51×10^{1}
y-Intercept: -1.68

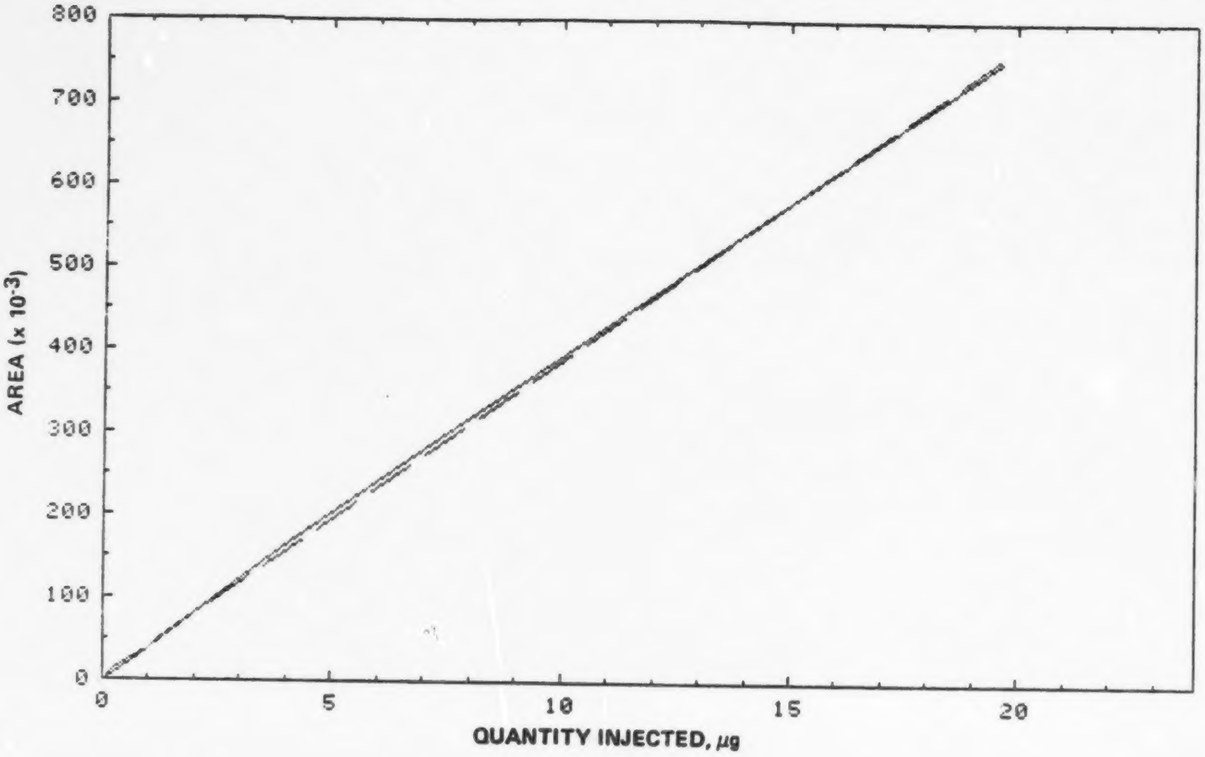

Figure C-33. Calibration curve for the determination of 2-methylphenol by HPLC/UV (280 nm).

Range: 0.39 - 20 µg
Correlation coefficient: 0.999
Slope: 3.93×10^1
y-Intercept: 1.28

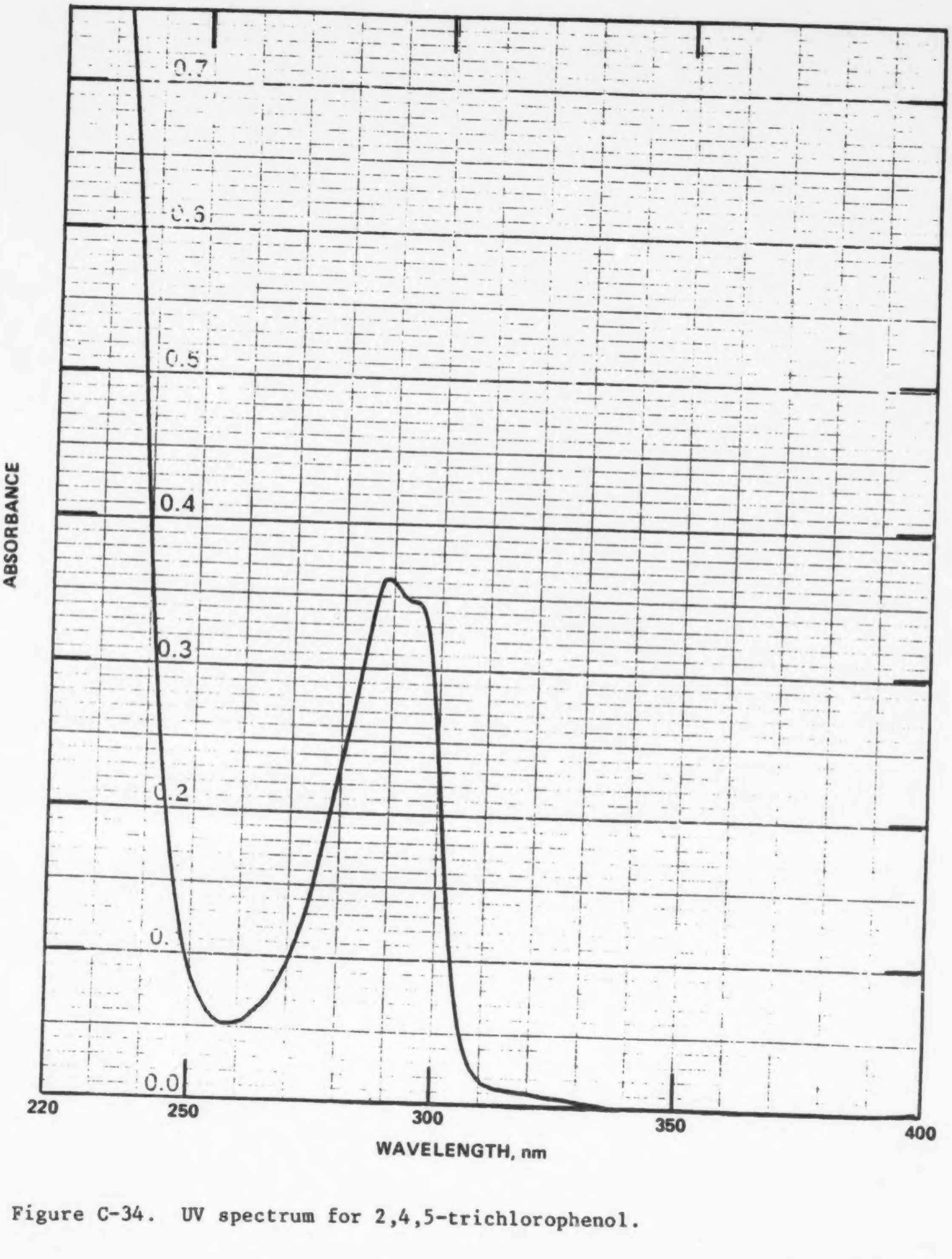

Figure C-34. UV spectrum for 2,4,5-trichlorophenol.

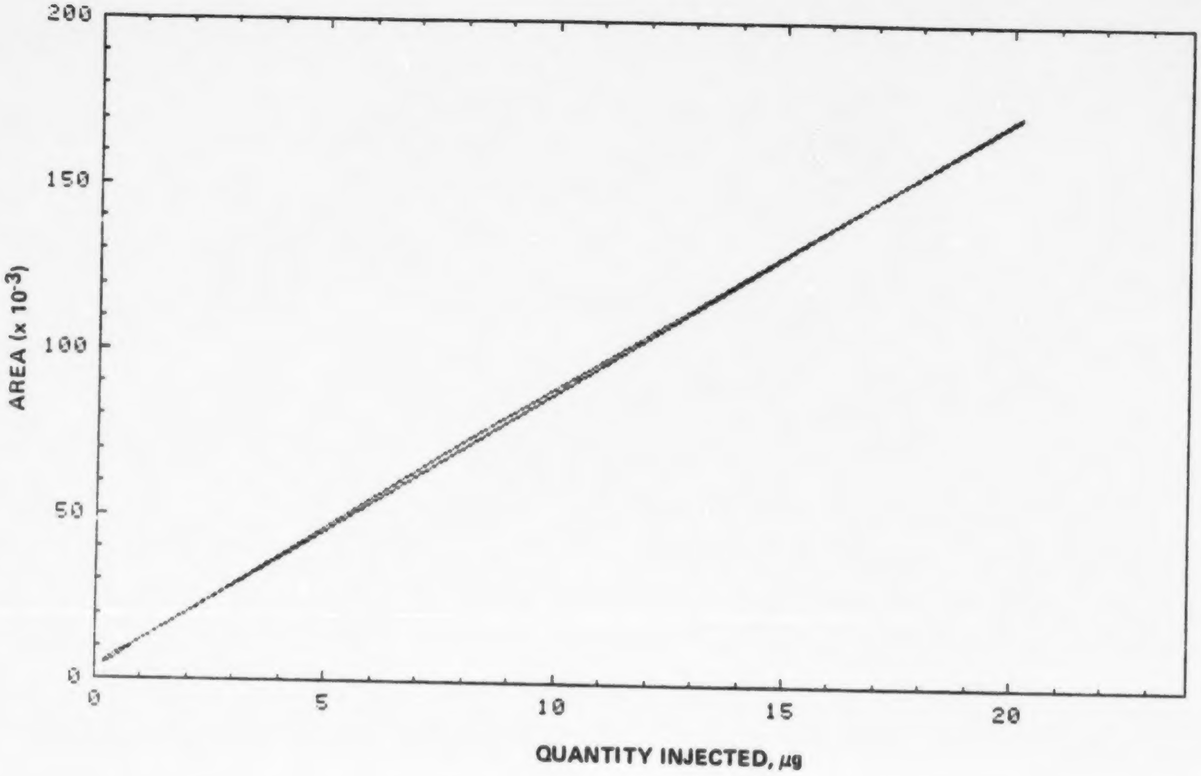

Figure C-35. Calibration curve for the determination of 2,4,5-trichlorophenol by HPLC/UV (254 nm).

Range: 0.40 - 20 µg
Correlation coefficient: 0.999
Slope: 8.44
y-Intercept: 2.83

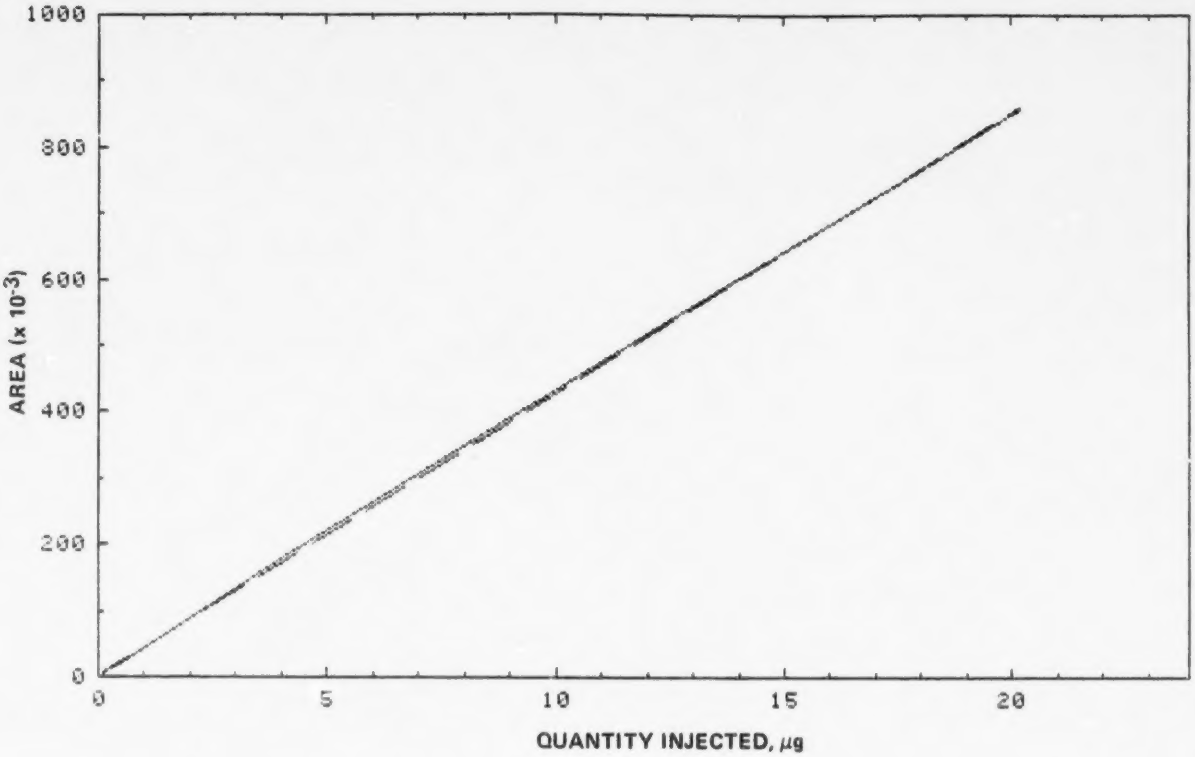

Figure C-36. Calibration curve for the determination of 2,4,5-trichlorophenol by HPLC/UV (280 nm).

Range: 0.40 - 20 µg
Correlation coefficient: 0.999
Slope: 4.26×10^1
y-Intercept: 1.84

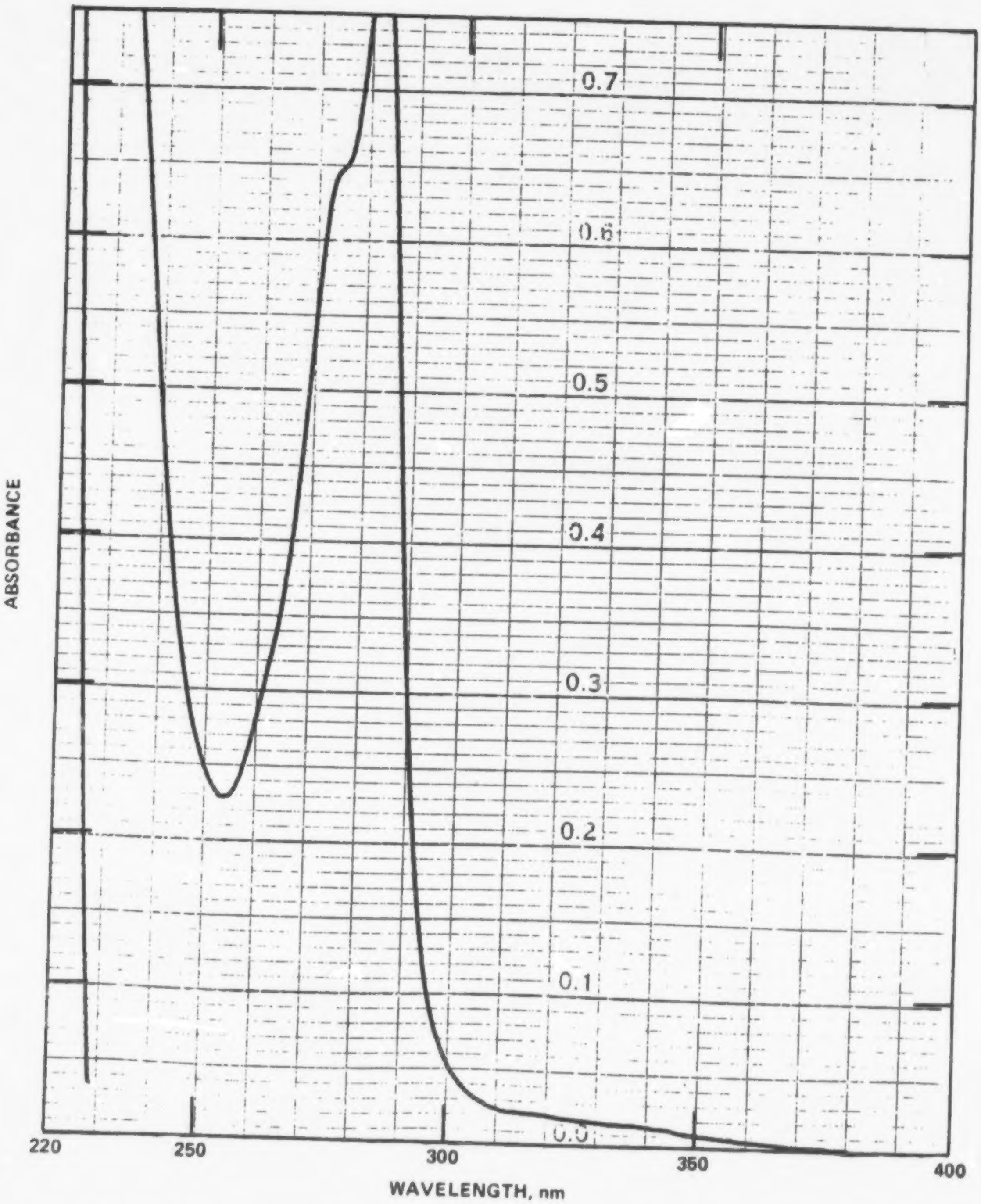

Figure C-37. UV spectrum for pentachlorophenol.

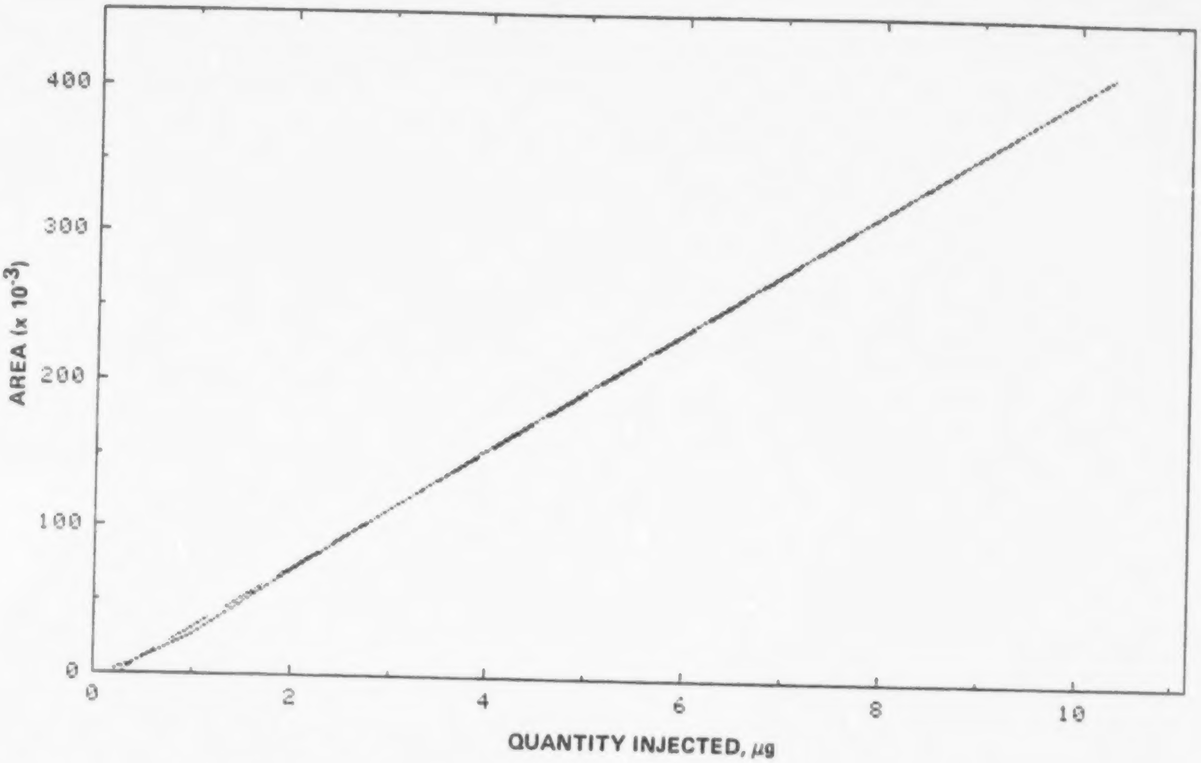

Figure C-38. Calibration curve for the determination of pentachlorophenol by HPLC/UV (254 nm).

Range: 0.41 - 10 μg
Correlation coefficient: 0.999
Slope: 4.08×10^1
y-Intercept: -9.27

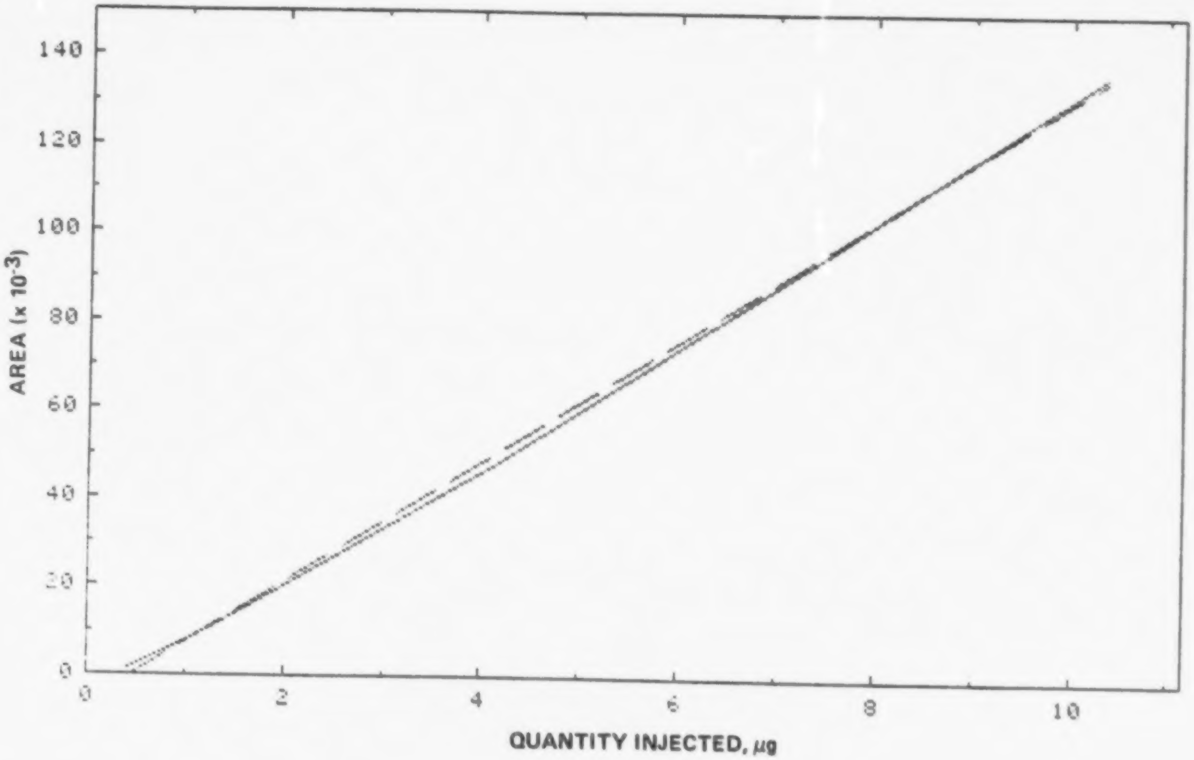

Figure C-39. Calibration curve for the determination of pentachlorophenol by HPLC/UV (280 nm).

Range: 1.0 - 10 µg
Correlation coefficient: 0.999
Slope: 1.37×10^1
y-Intercept: -6.23

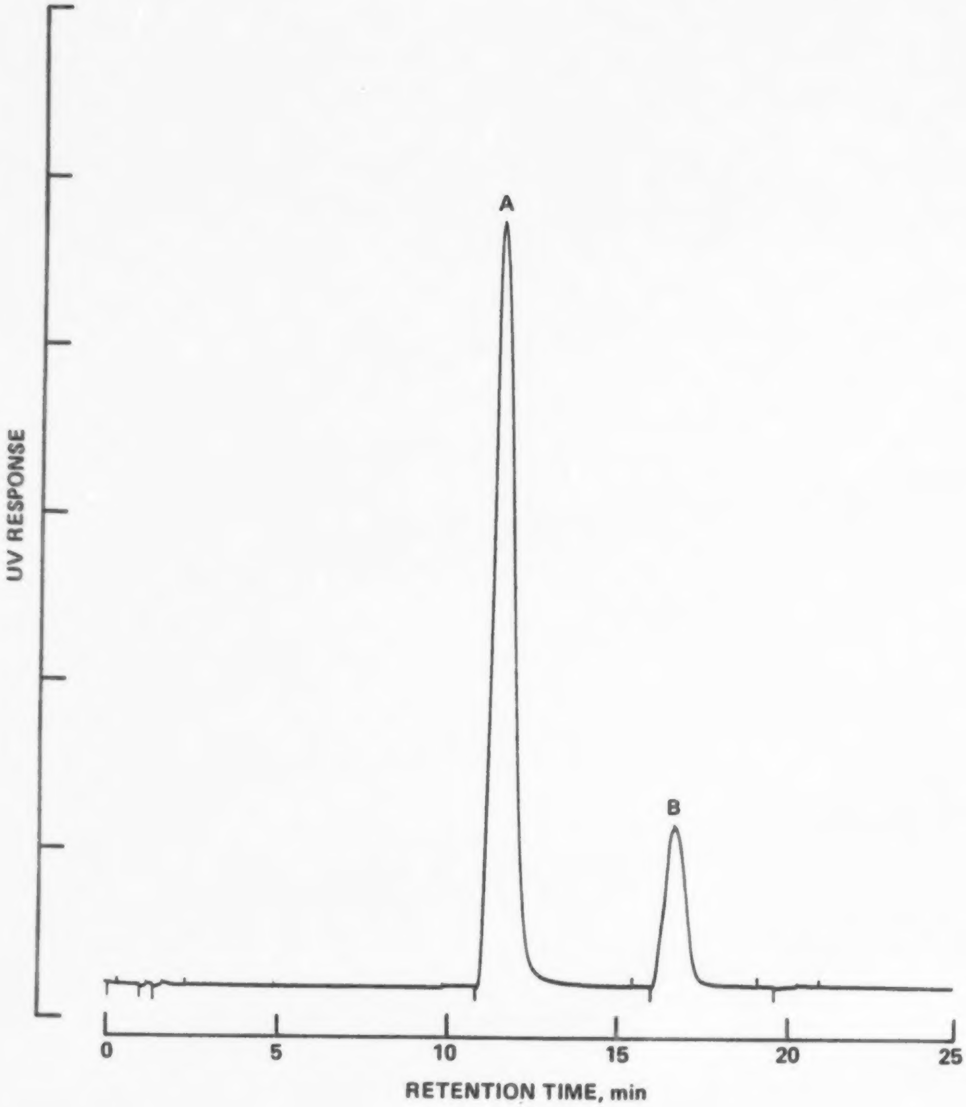

Figure C-40. Chromatogram by HPLC/UV (254 nm) for

(A) phenacetin(t_R = 11.9 min) and
(B) benzenethiol(t_R = 16.8 min).

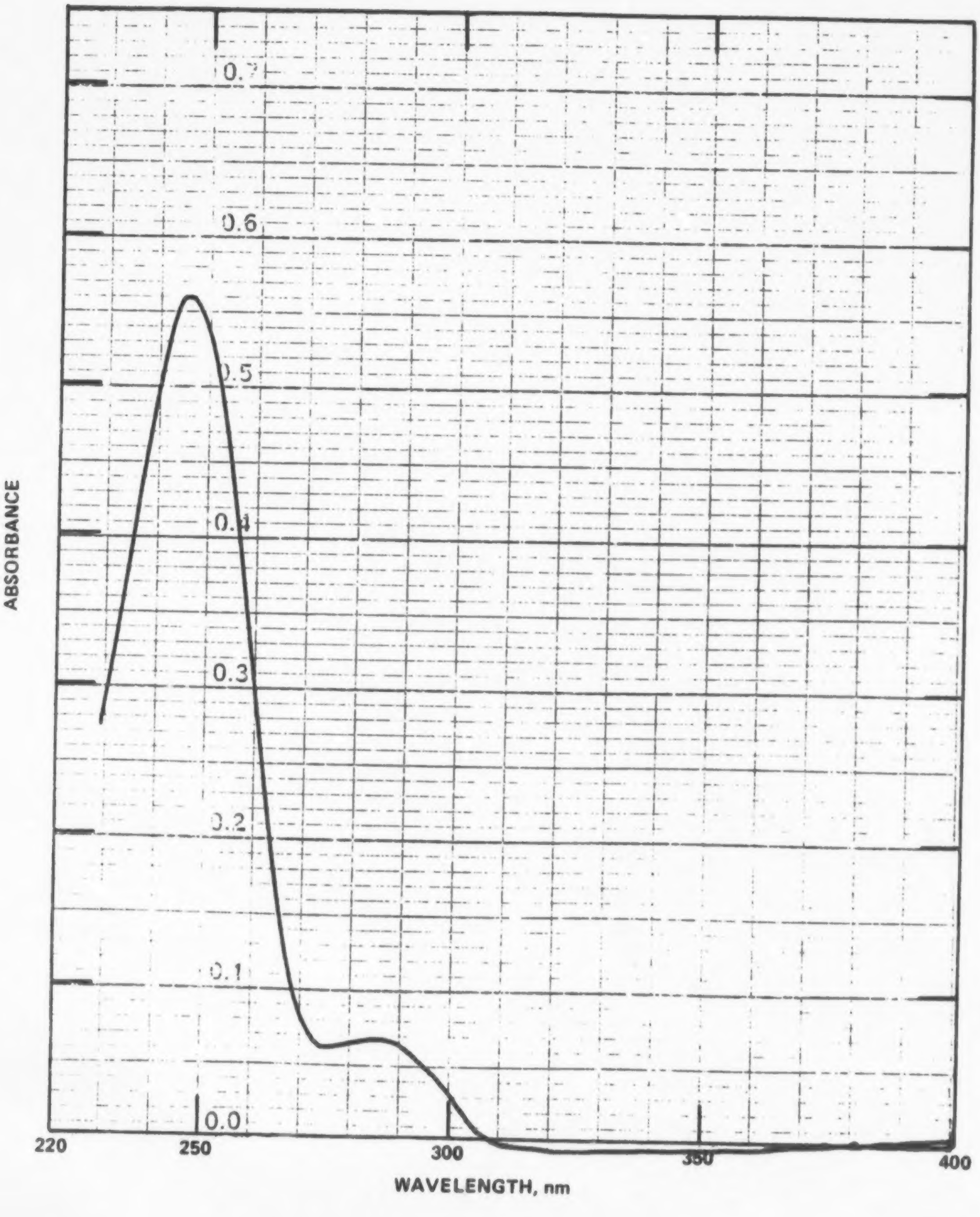

Figure C-41. UV spectrum for phenacetin.

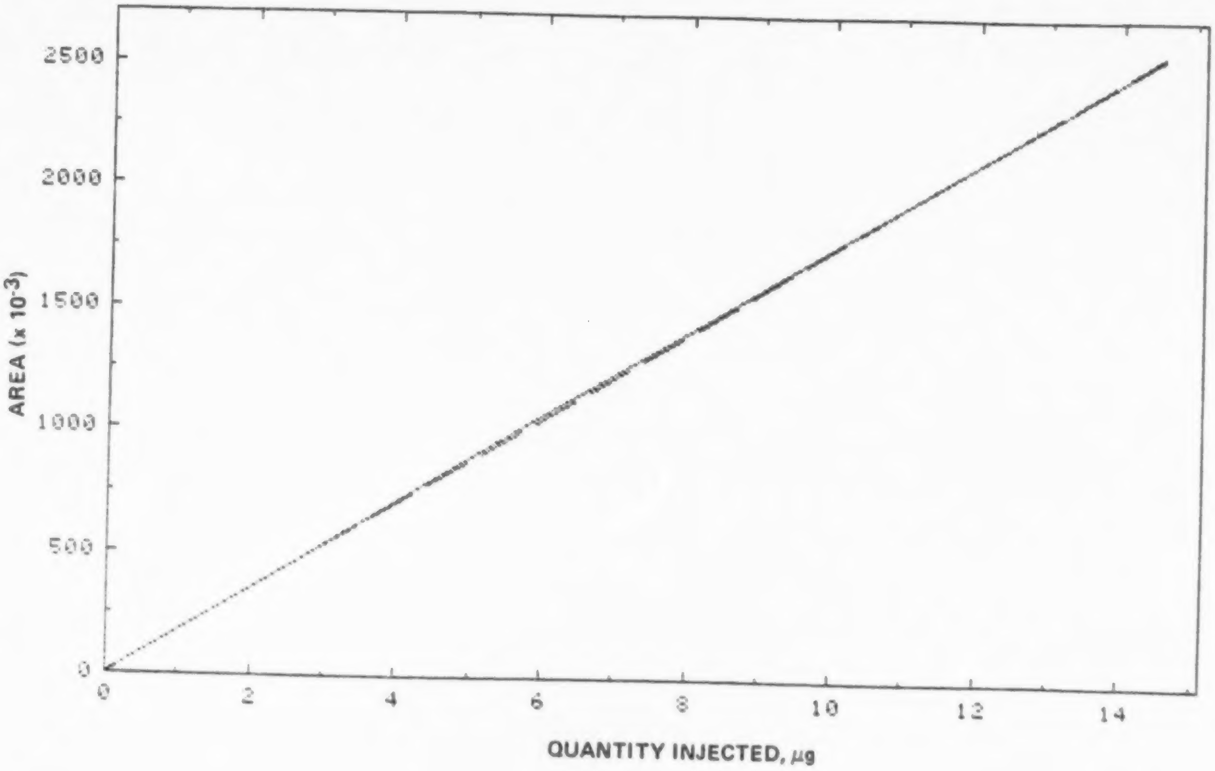

Figure C-42. Calibration curve for the determination of phenacetin by HPLC/UV (254 nm).

Range: 0.058 - 15 µg
Correlation coefficient: 0.999
Slope: 1.75×10^2
y-Intercept: 3.35

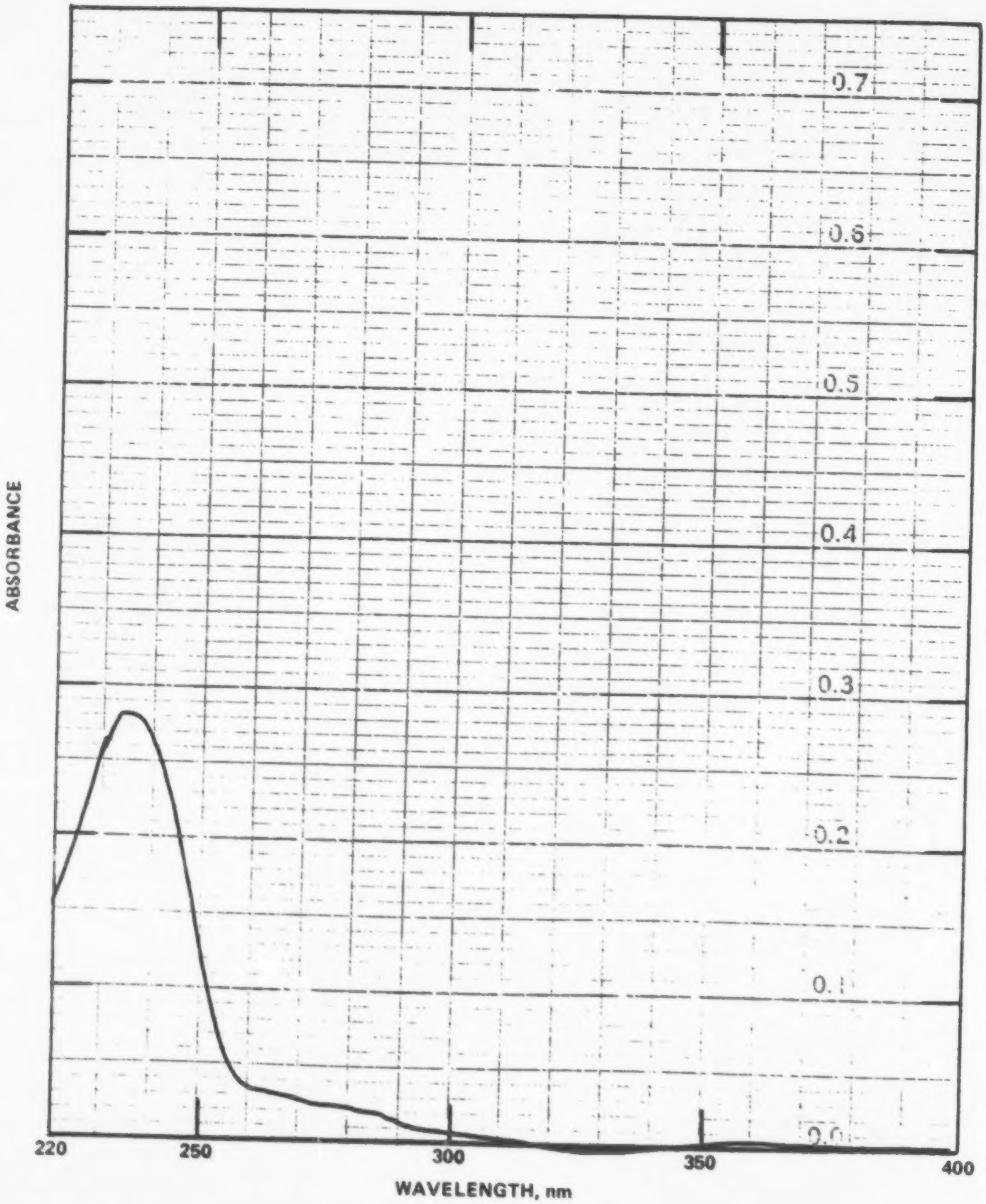

Figure C-43. UV spectrum for benzenethiol.

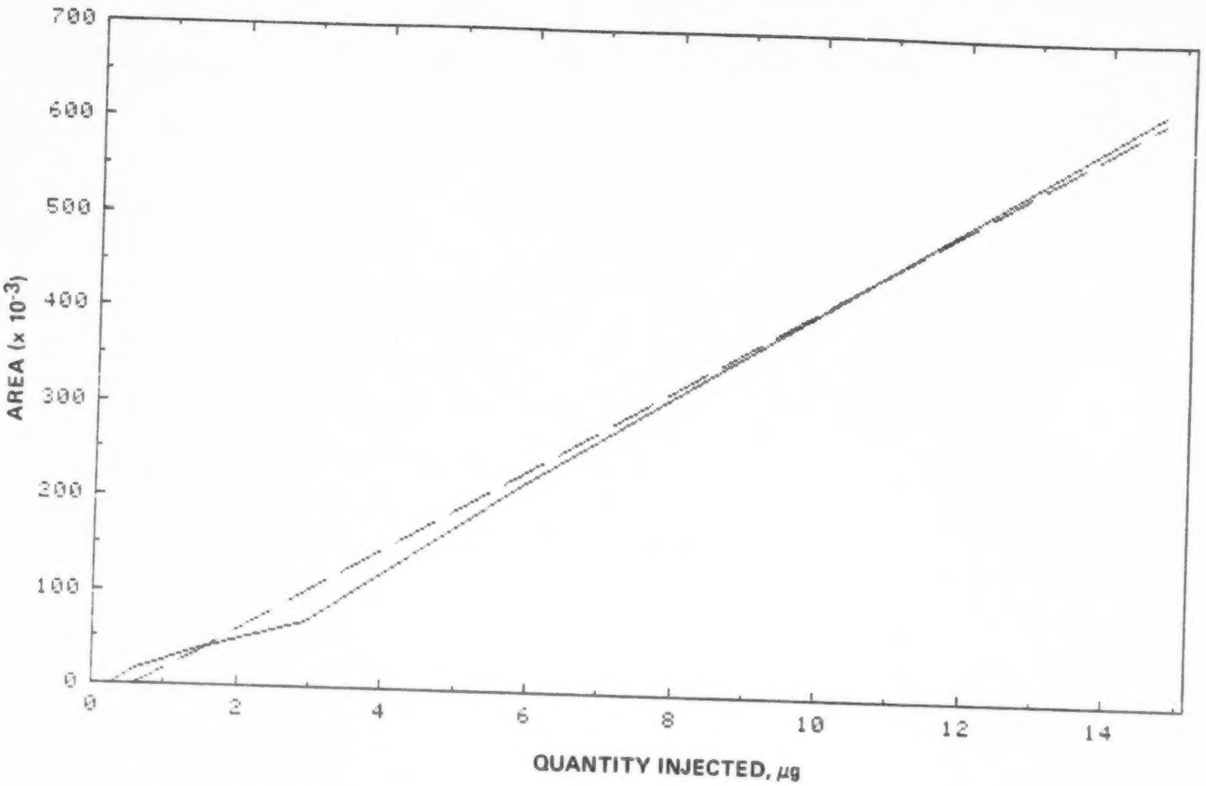

Figure C-44. Calibration curve for the determination of benzenethiol by HPLC/UV (254 nm).

Range: 1.5 - 15 µg
Correlation coefficient: 0.997
Slope: 4.36×10^1
y-Intercept: -2.64×10^1

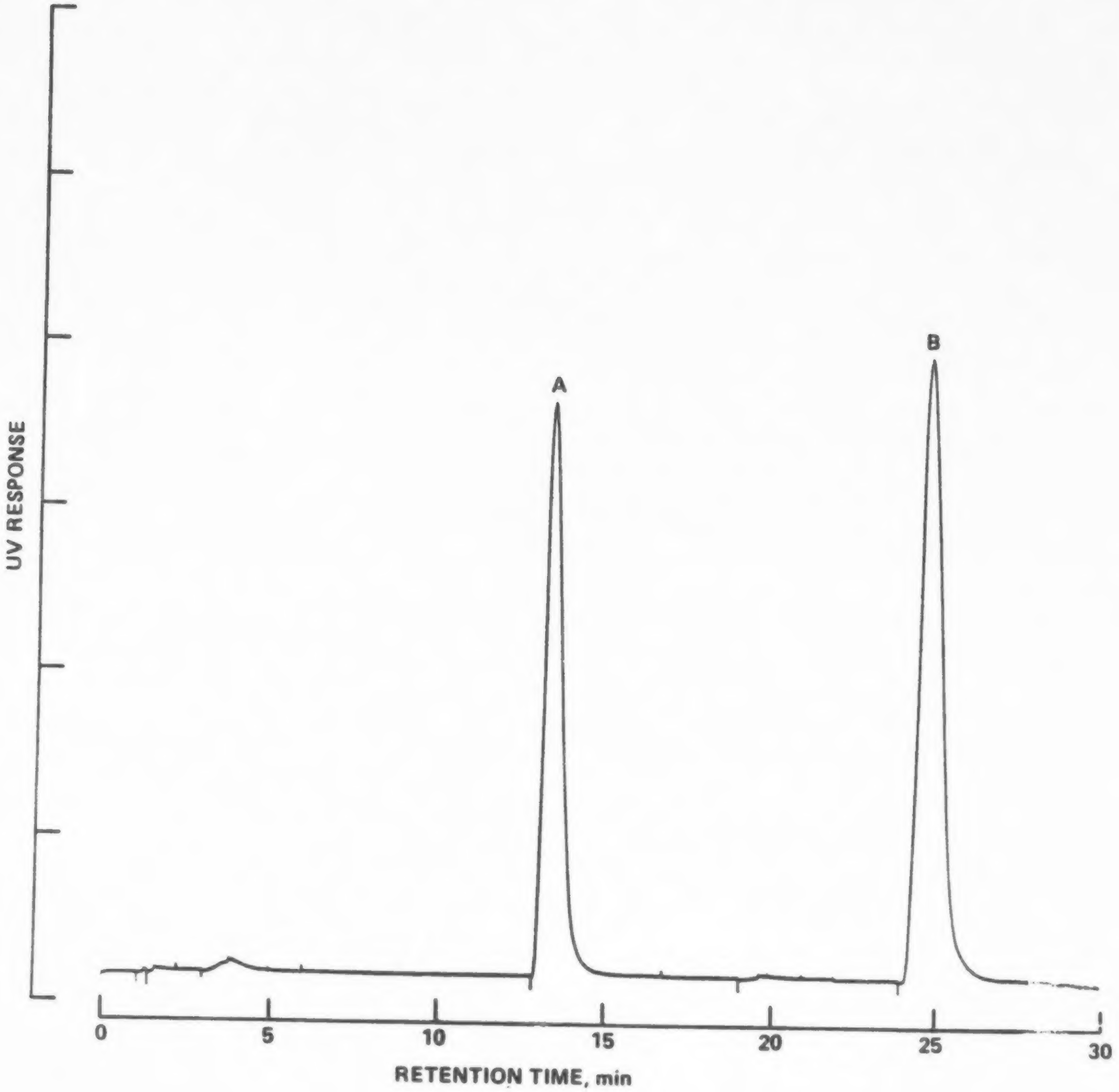

Figure C-45. Chromatogram by HPLC/UV for

(A) melphalan (254 nm) (t_R = 13.3 min) and
(B) benzaldehyde-DNPH (378 nm) (t_R = 24.7 min).

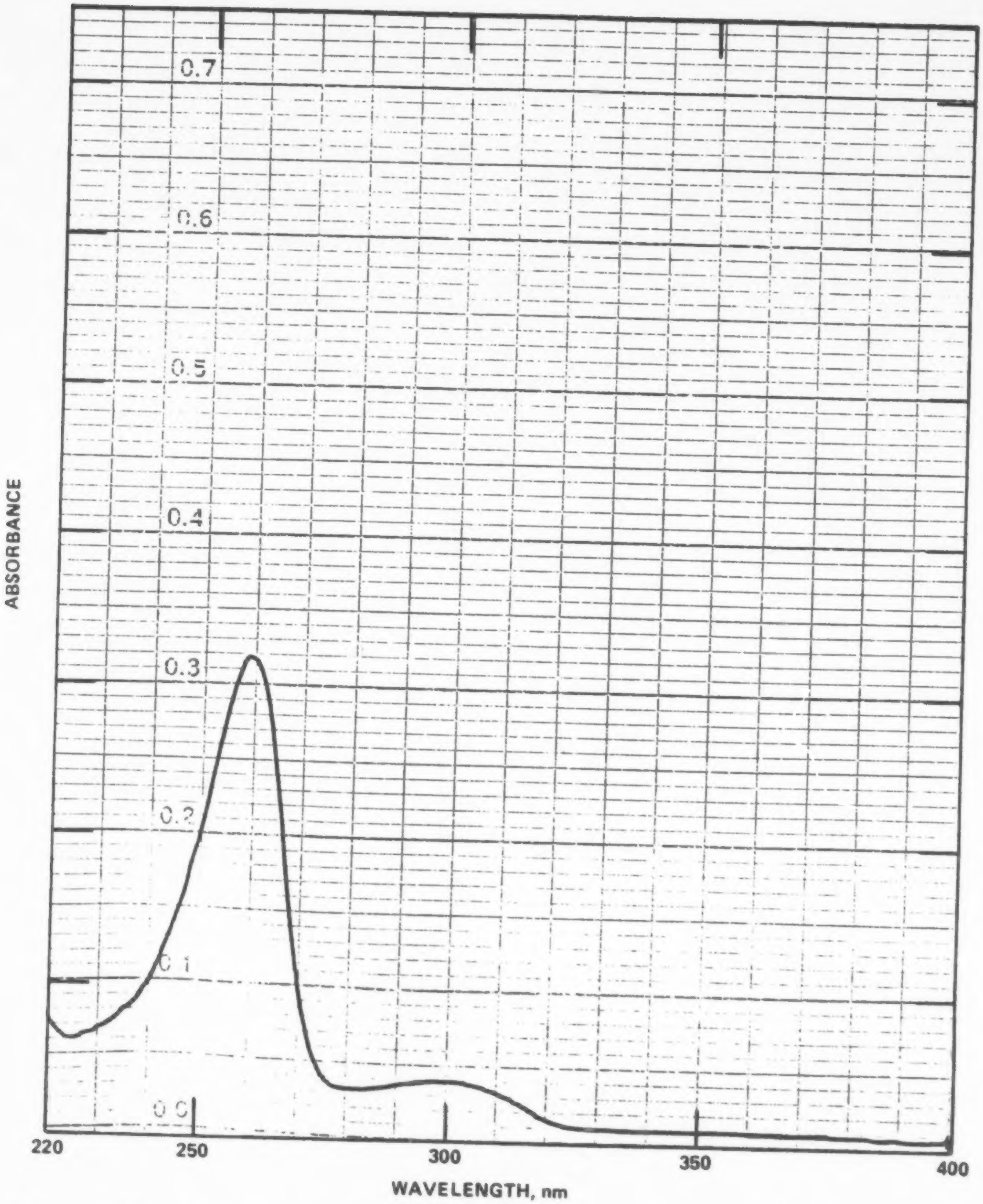

Figure C-46. UV spectrum for melphalan.

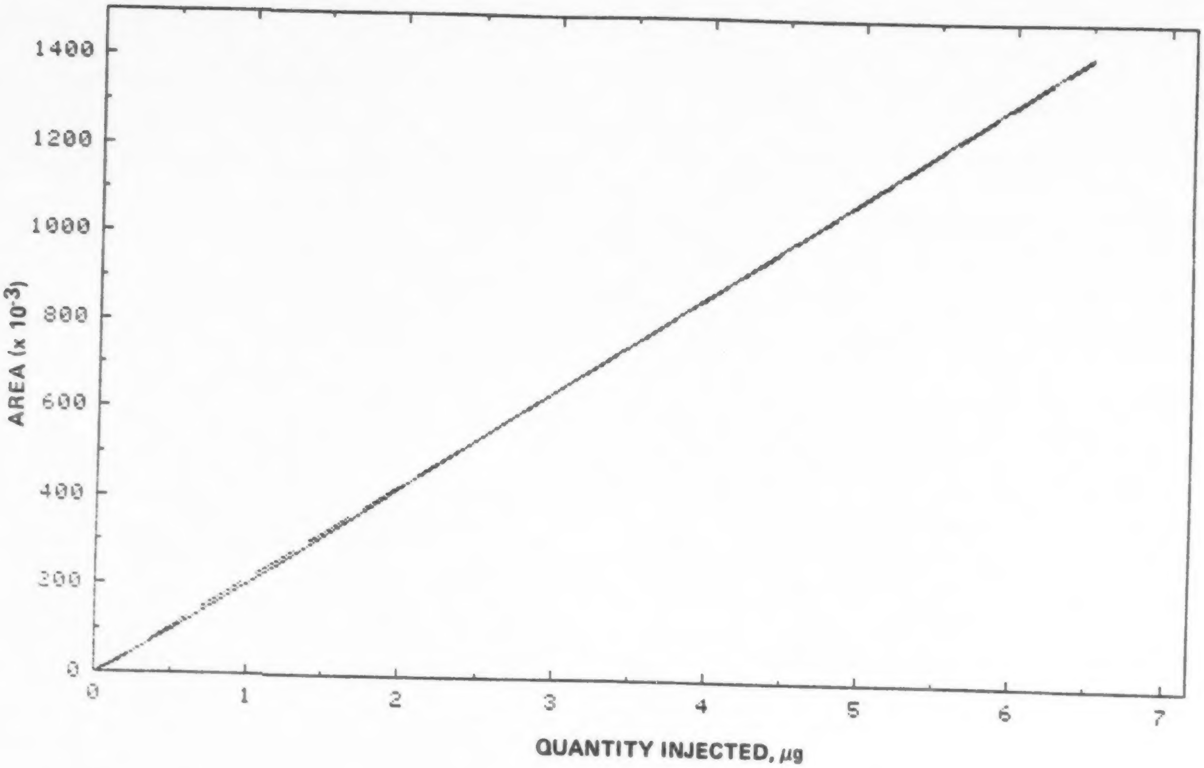

Figure C-47. Calibration curve for the determination of melphalan by HPLC/UV (254 nm).

Range: 0.13 - 6.5 µg
Correlation coefficient: 0.999
Slope: 2.20×10^2
y-Intercept: -6.72

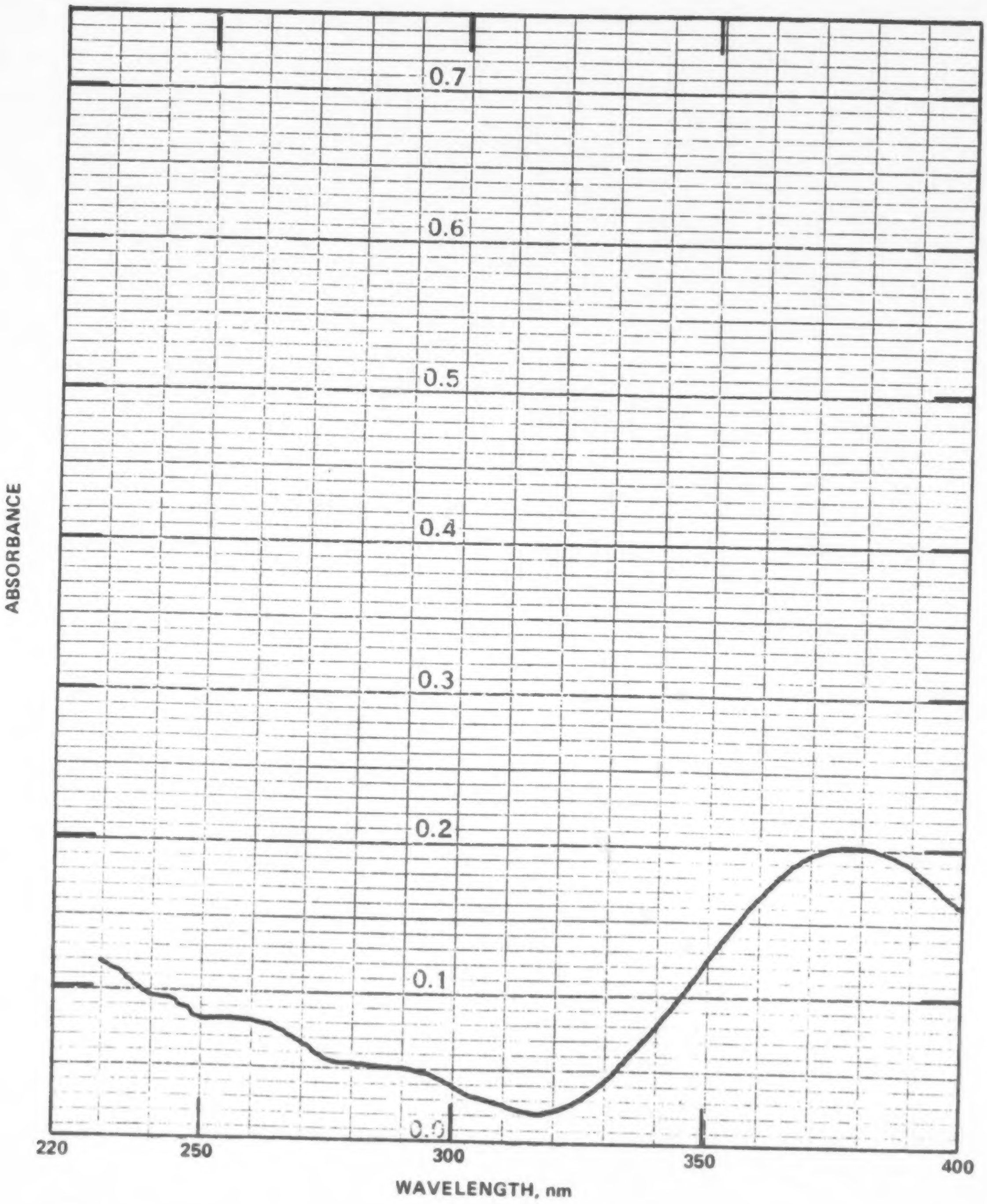

Figure C-48. UV spectrum for benzaldehyde-DNPH.

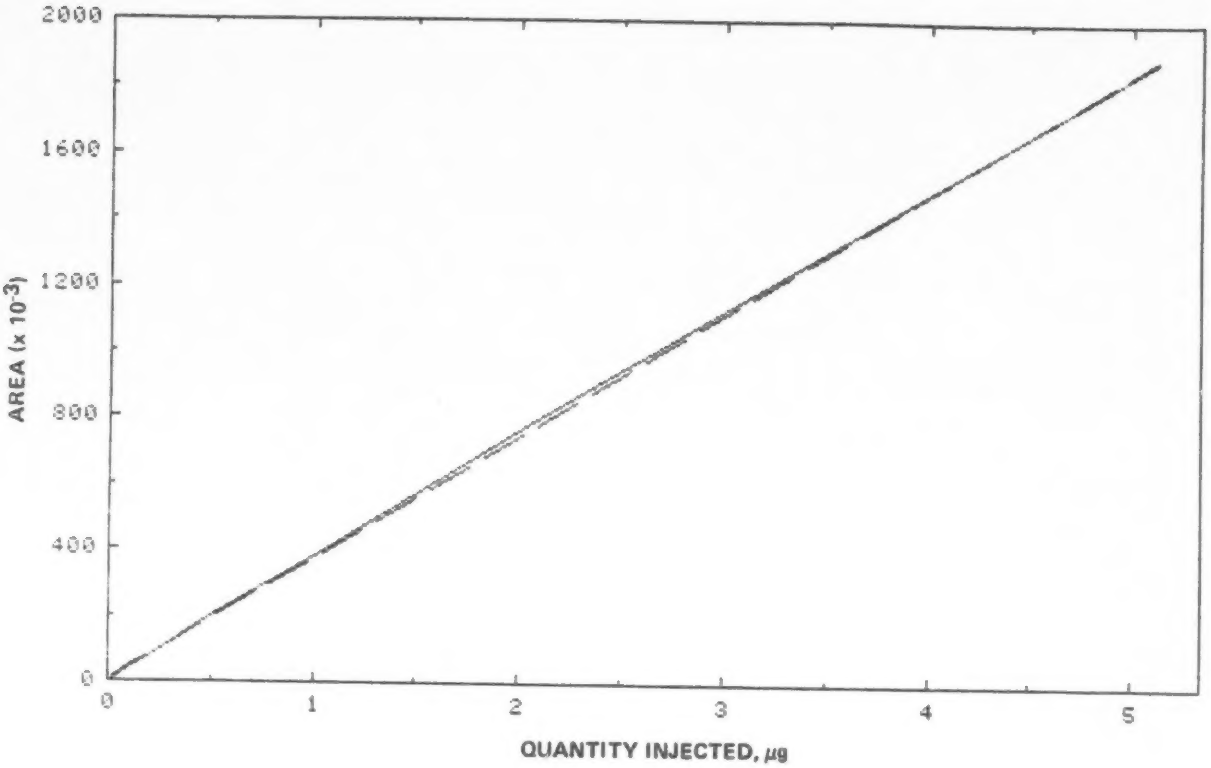

Figure C-49. Calibration curve for the determination of benzaldehyde-DNPH by HPLC/UV (378 nm).

Range: 0.51 - 5.1 µg
Correlation coefficient: 0.999
Slope: 3.69×10^2
y-Intercept: 6.23

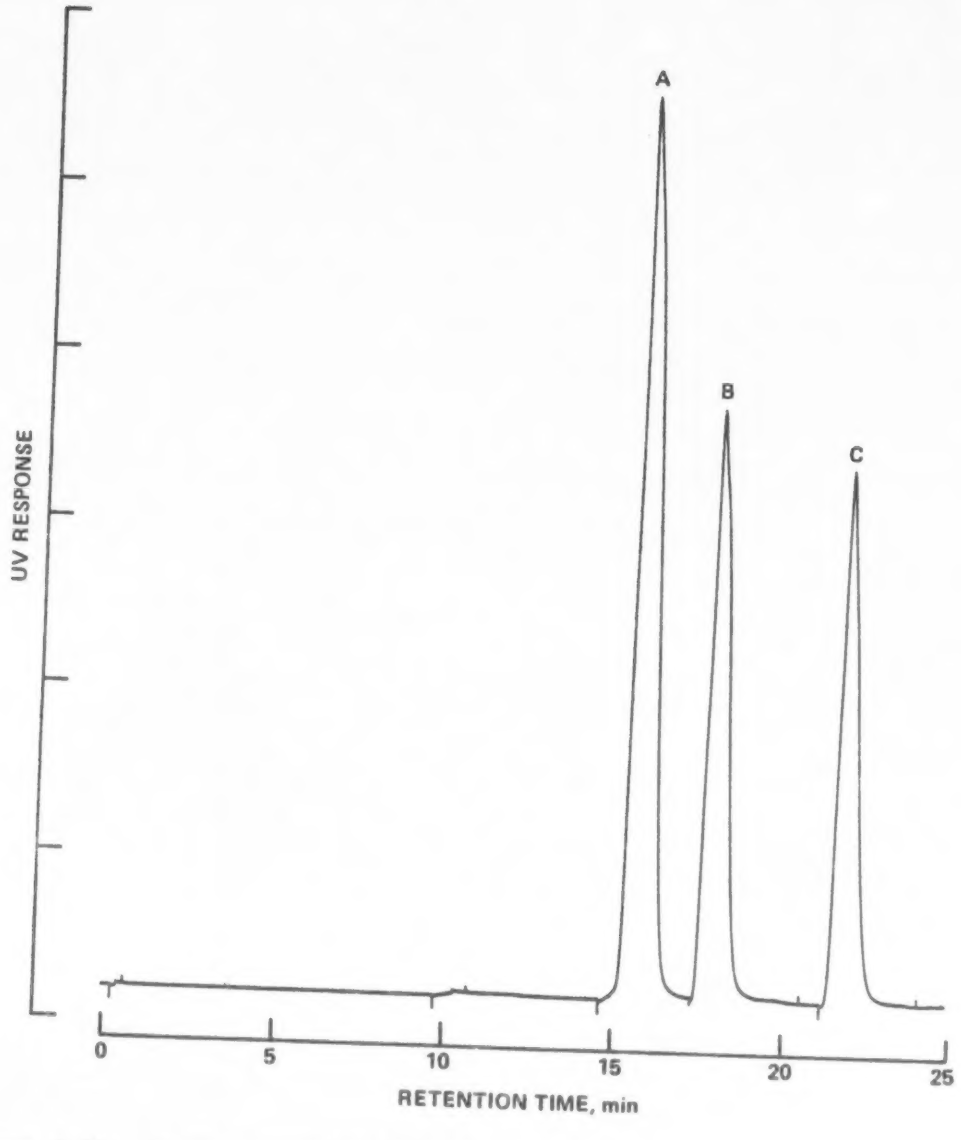

Figure C-50. Chromatogram by HPLC/UV (254 nm) for

(A) formaldehyde-DNPH(t_R = 17.0 min),
(B) acetaldehyde-DNPH(t_R = 19.2 min), and
(C) crotonaldehyde-DNPH(t_R = 23.0 min).

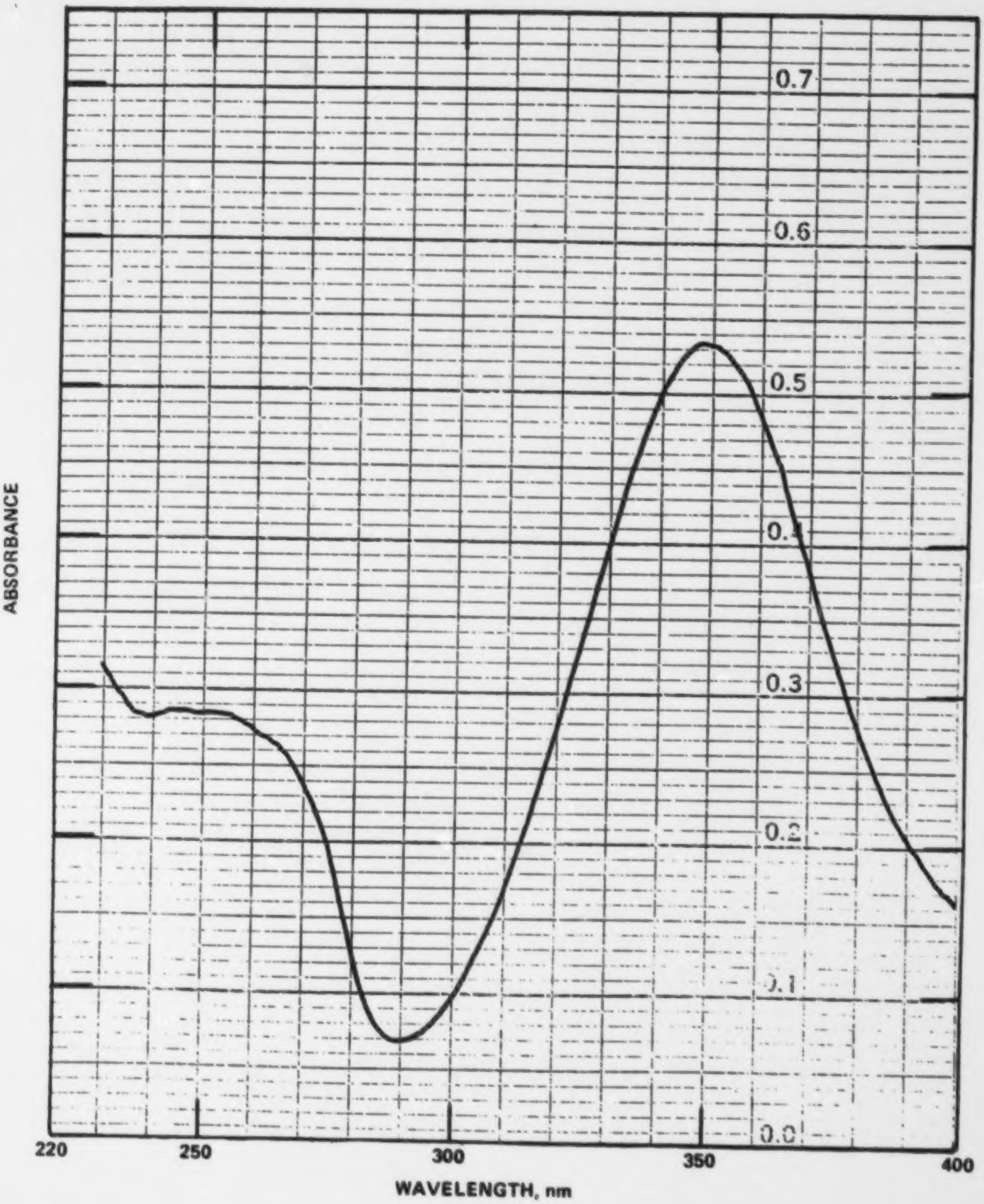

Figure C-51. UV spectrum for formaldehyde-DNPH.

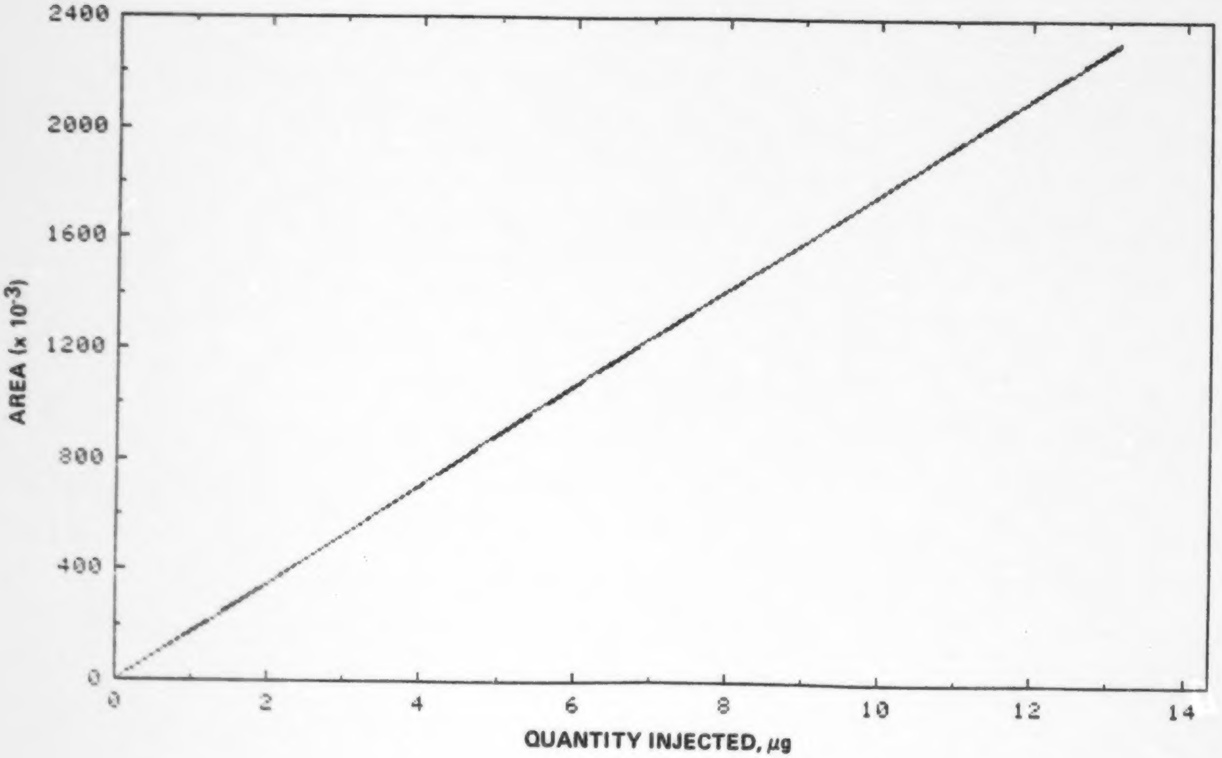

Figure C-52. Calibration curve for the determination of formaldehyde-DNPH by HPLC/UV (254 nm).

Range: 0.052 - 10 μg
Correlation coefficient: 0.999
Slope: 1.77×10^2
y-Intercept: 1.55

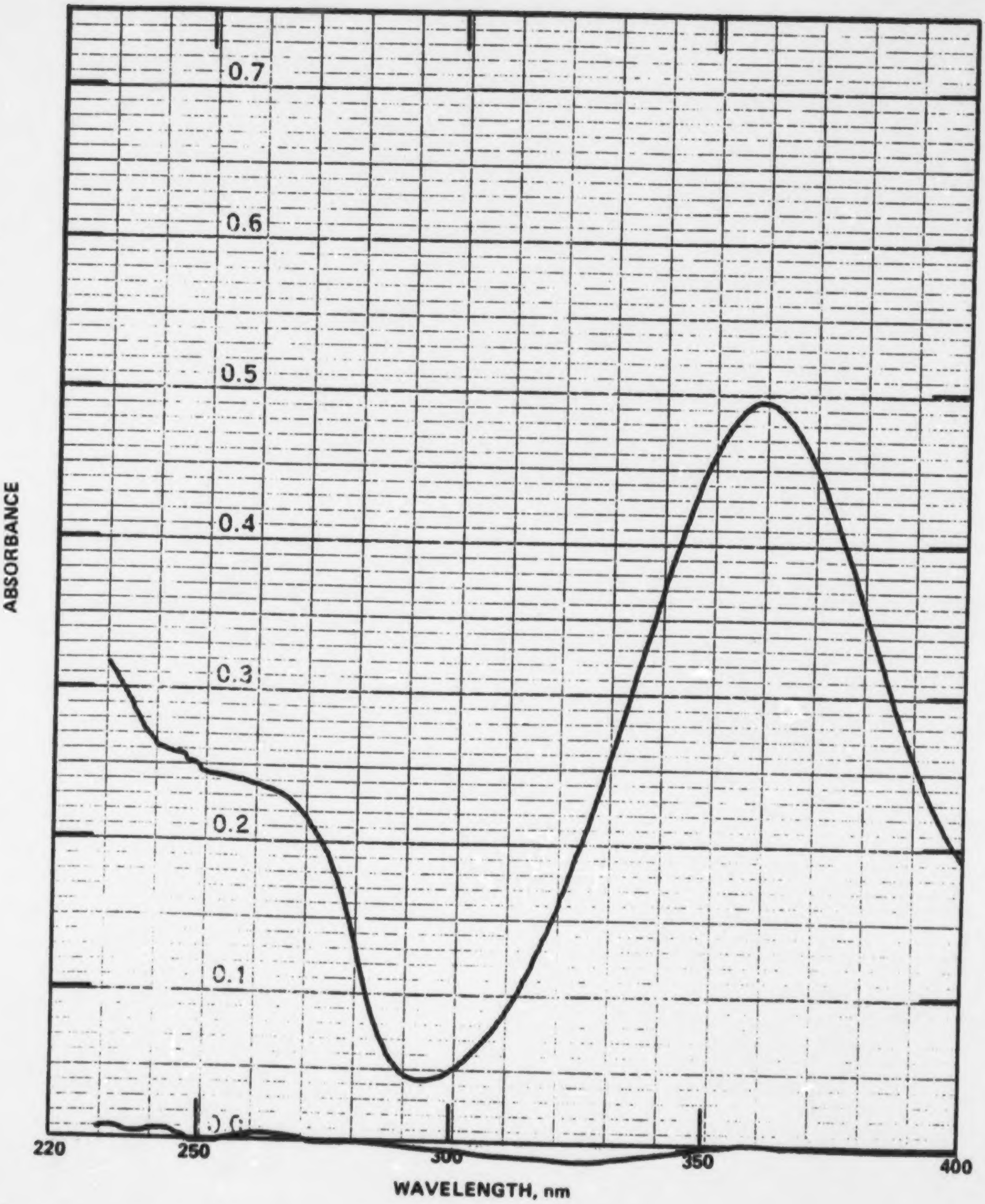

Figure C-53. UV spectrum for acetaldehyde-DNPH.

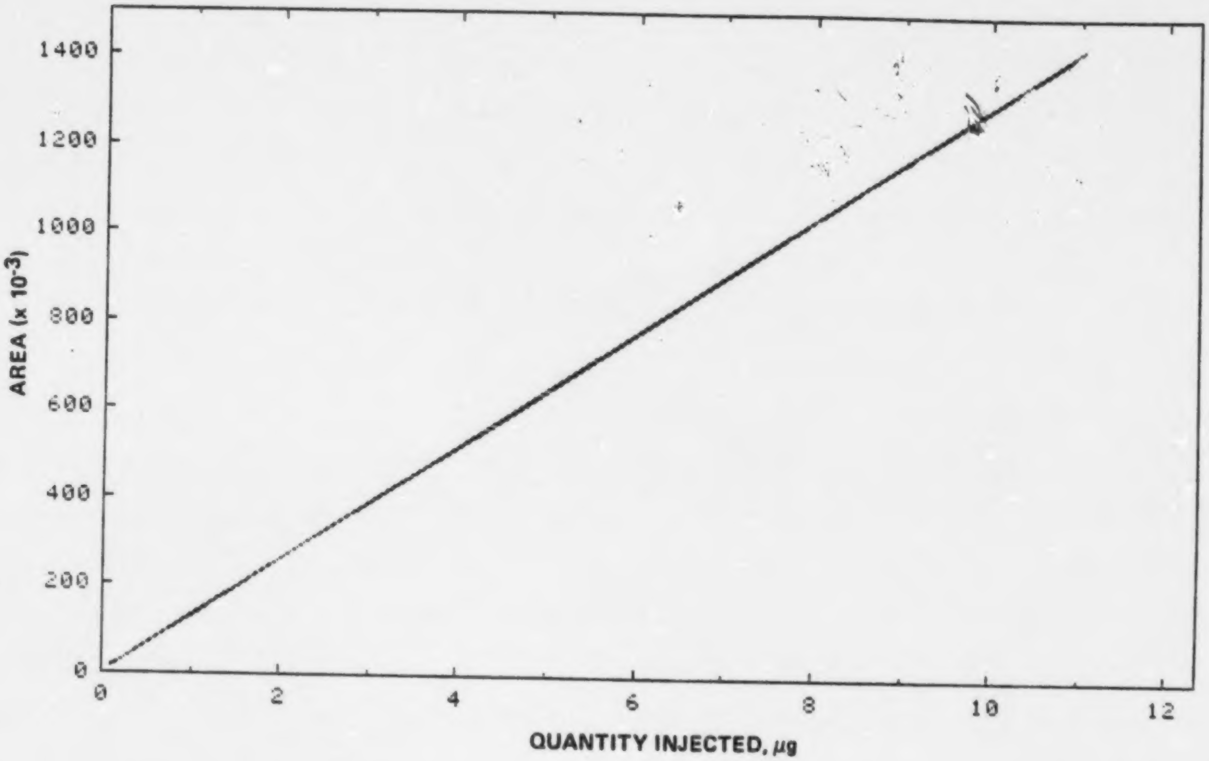

Figure C-54. Calibration curve for the determination of acetaldehyde-DNPH by HPLC/UV (254 nm).

Range: 0.110 - 16 µg
Correlation coefficient: 0.999
Slope: 1.29 x 10^2
y-Intercept: 1.81

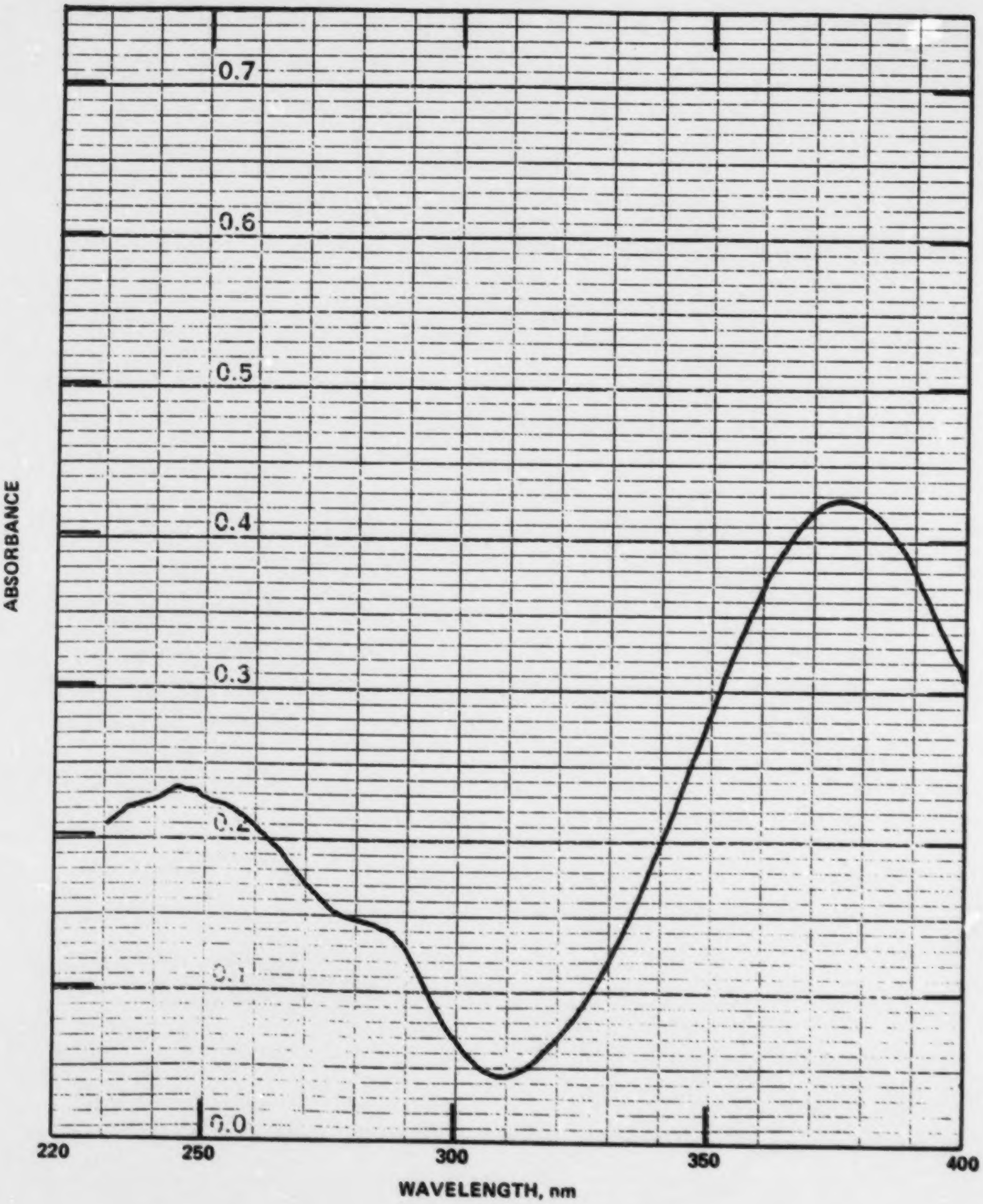

Figure C-55. UV spectrum for crotonaldehyde-DNPH.

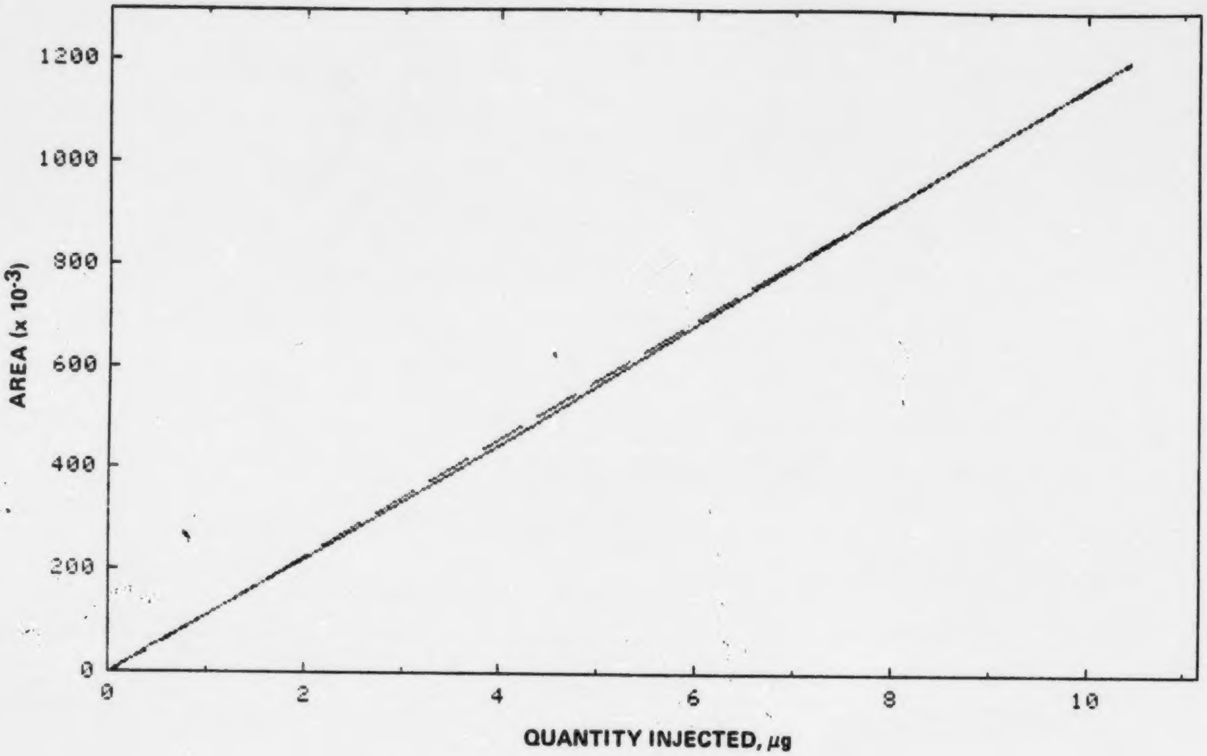

Figure C-56. Calibration curve for the determination of crotonaldehyde-DNPH by HPLC/UV (254 nm).

Range: 0.10 - 10 μg
Correlation coefficient: 0.999
Slope: 1.15 x 10^2
y-Intercept: -3.75

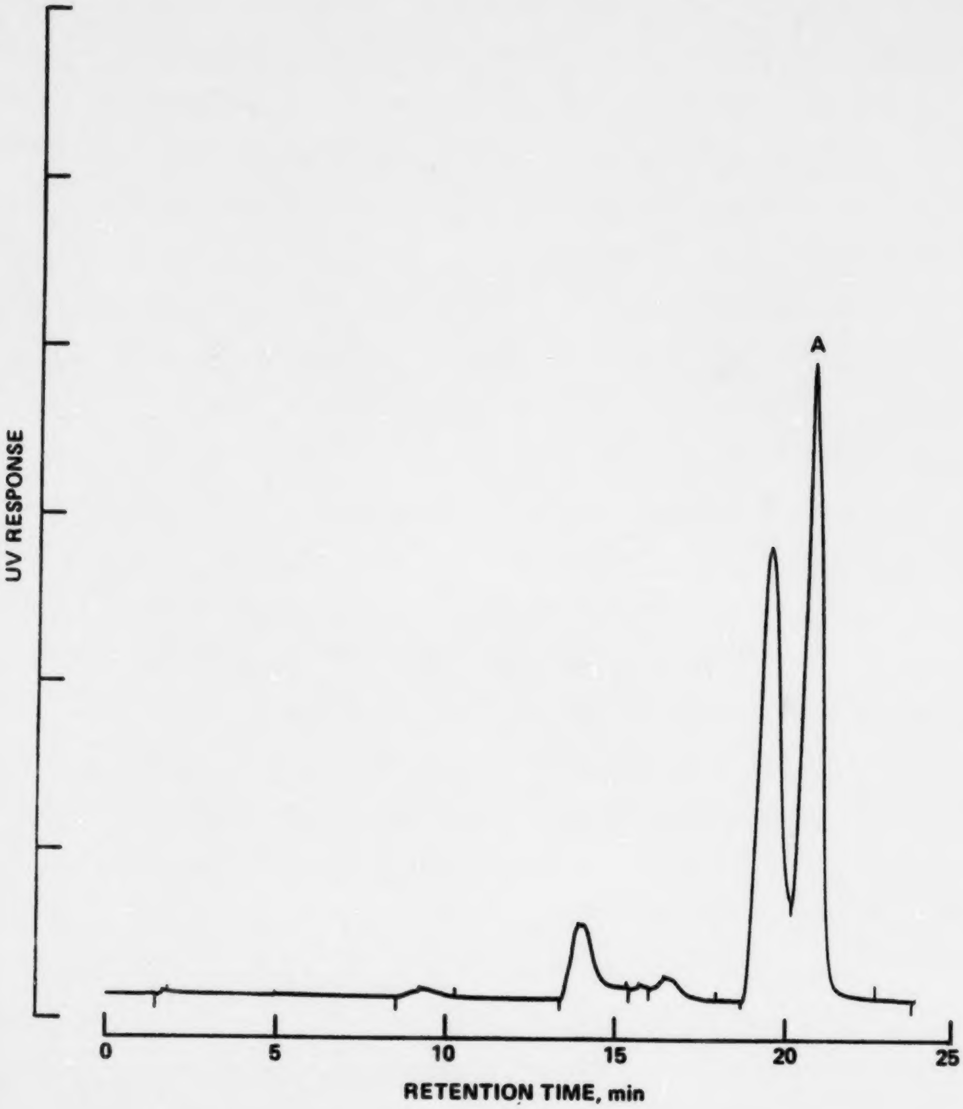

Figure C-57. Chromatogram by HPLC/UV (254 nm) for chloroacetaldehyde-DNPH.

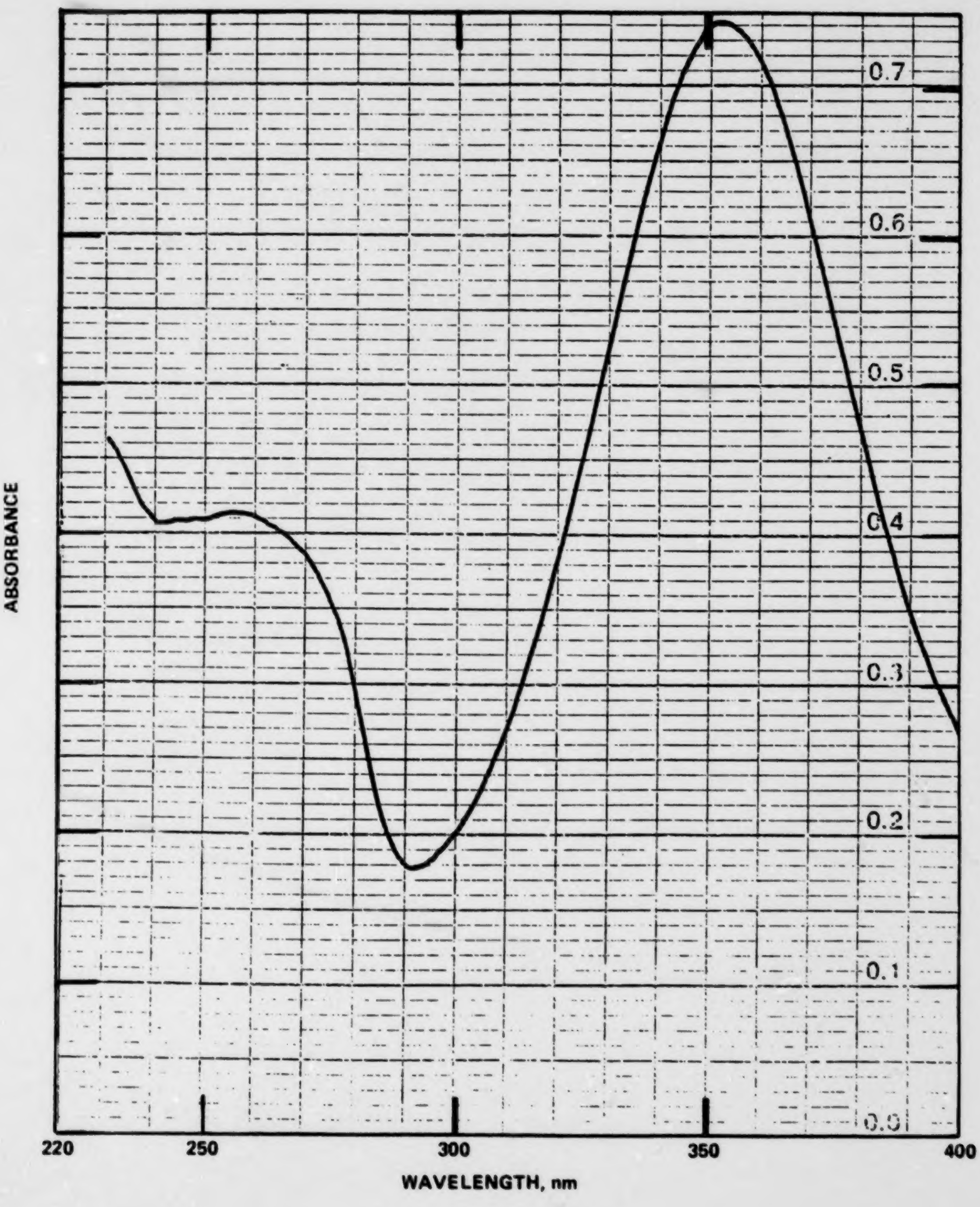

Figure C-58. UV spectrum for chloroacetaldehyde-DNPH.

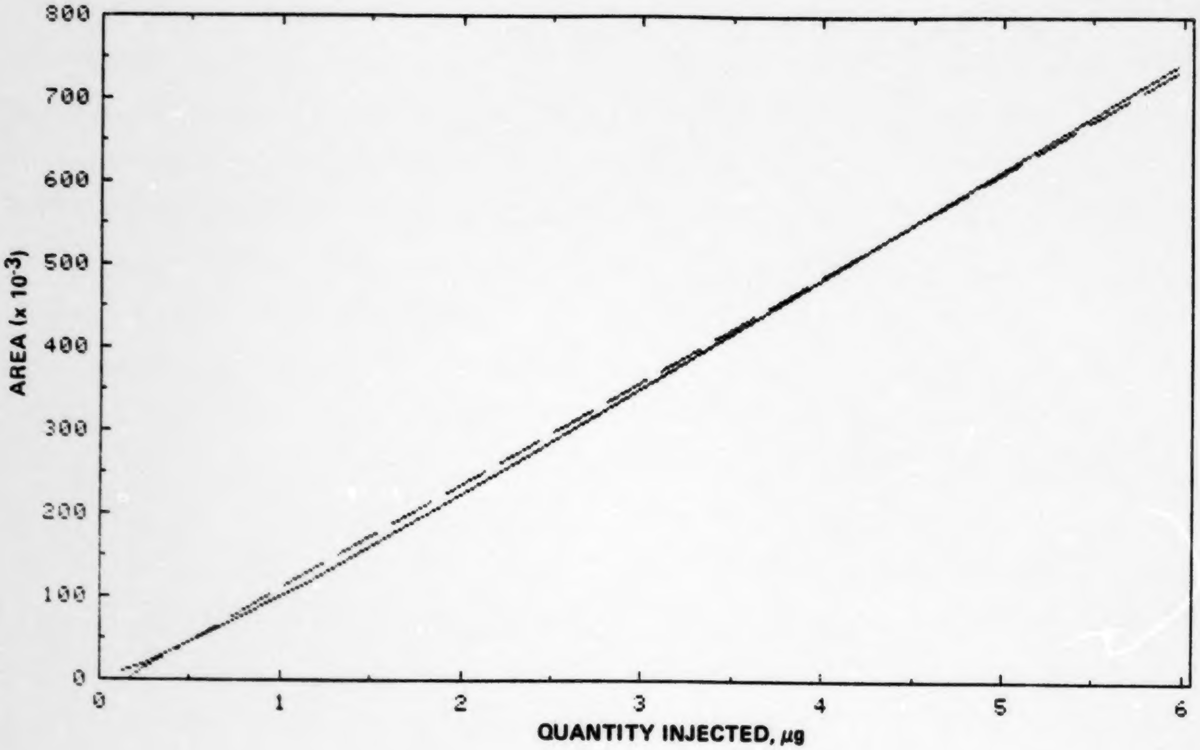

Figure C-59. Calibration curve for the determination of chloroacetaldehyde-DNPH by HPLC/UV (254 nm).

Range: 0.60 - 6.0 µg
Correlation coefficient: 0.999
Slope: 1.27×10^2
y-Intercept: -1.76×10^1

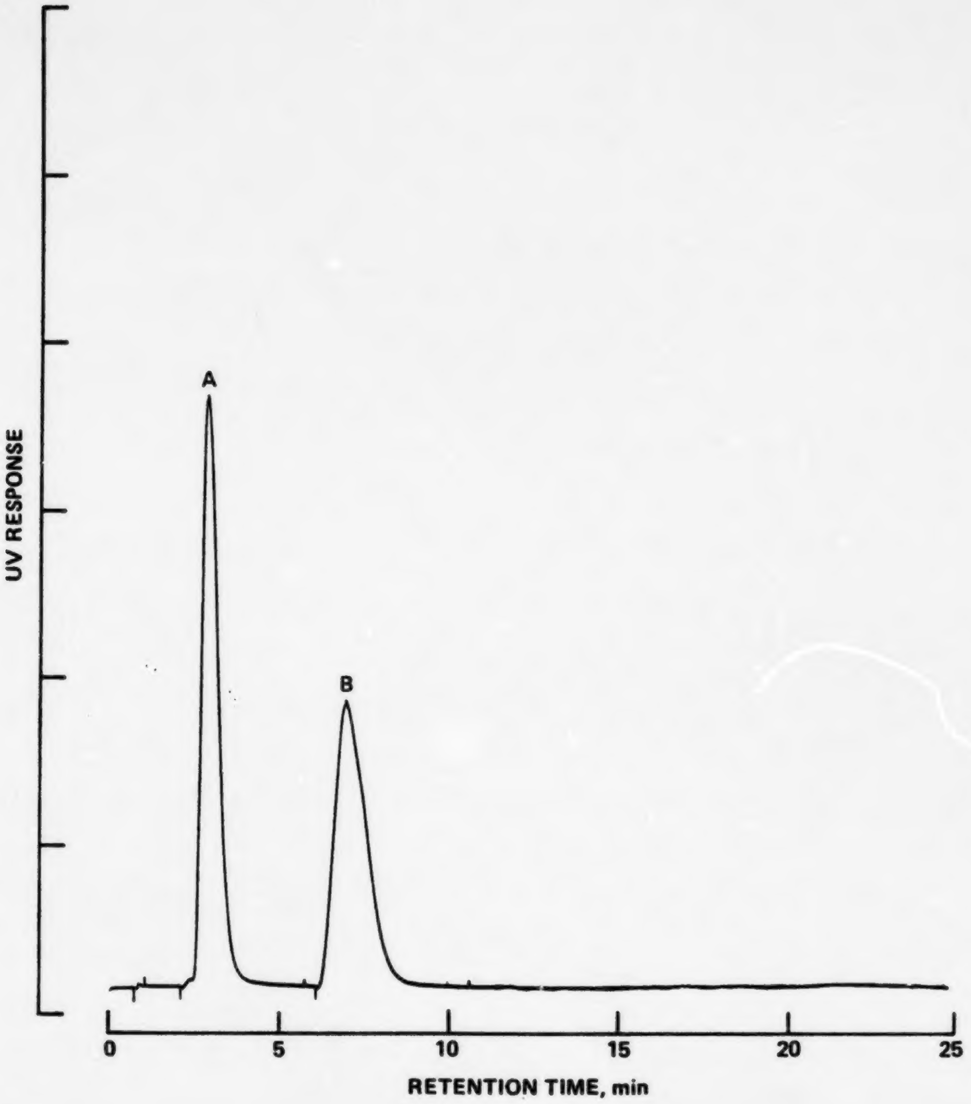

Figure C-60. Chromatogram by HPLC/UV (254 nm) for

(A) 2,4-dinitrophenol(t_R = 2.8 min) and
(B) 4,6-dinitro-o-cresol(t_R = 6.8 min).

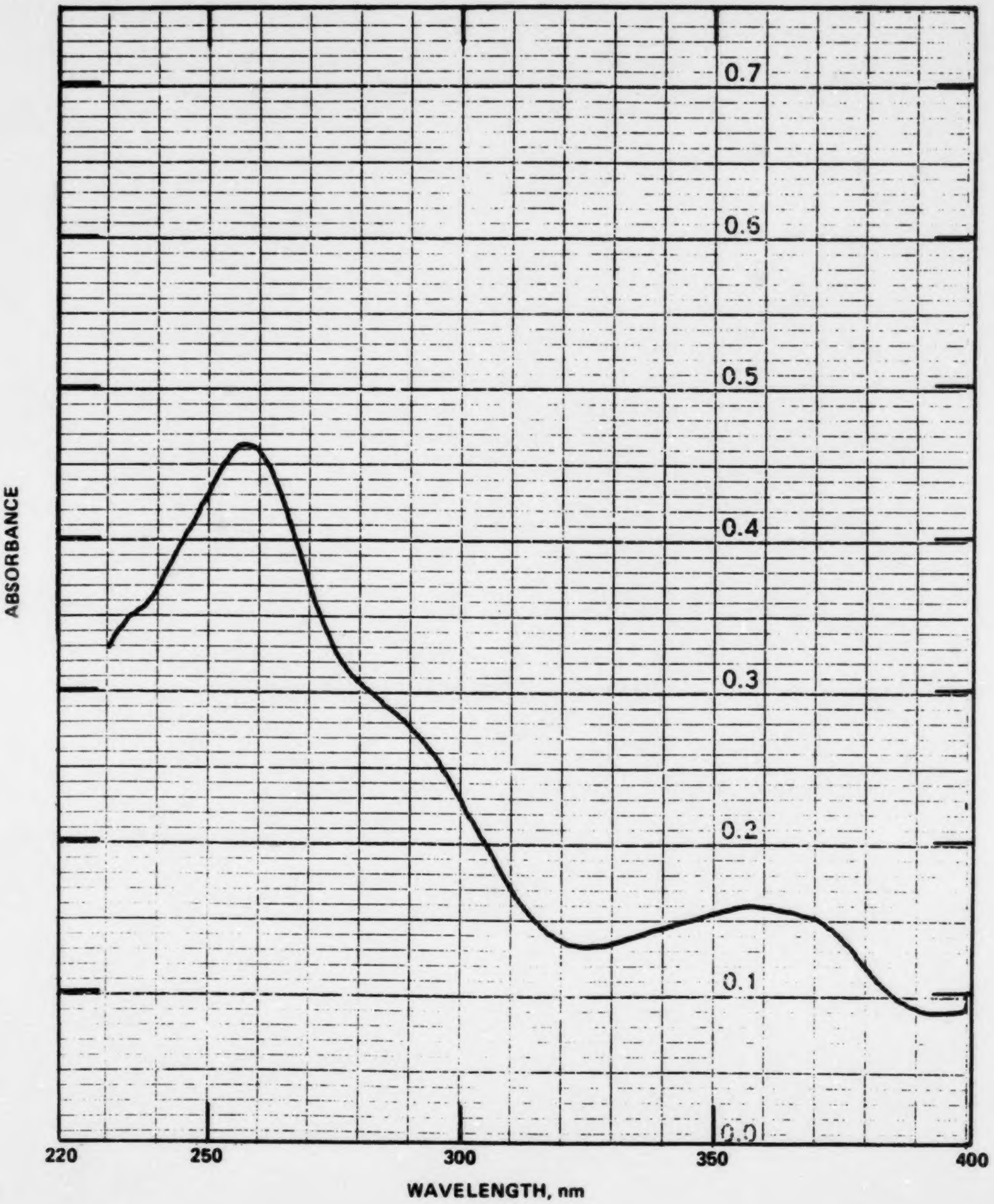

Figure C-61. UV spectrum for 2,4-dinitrophenol.

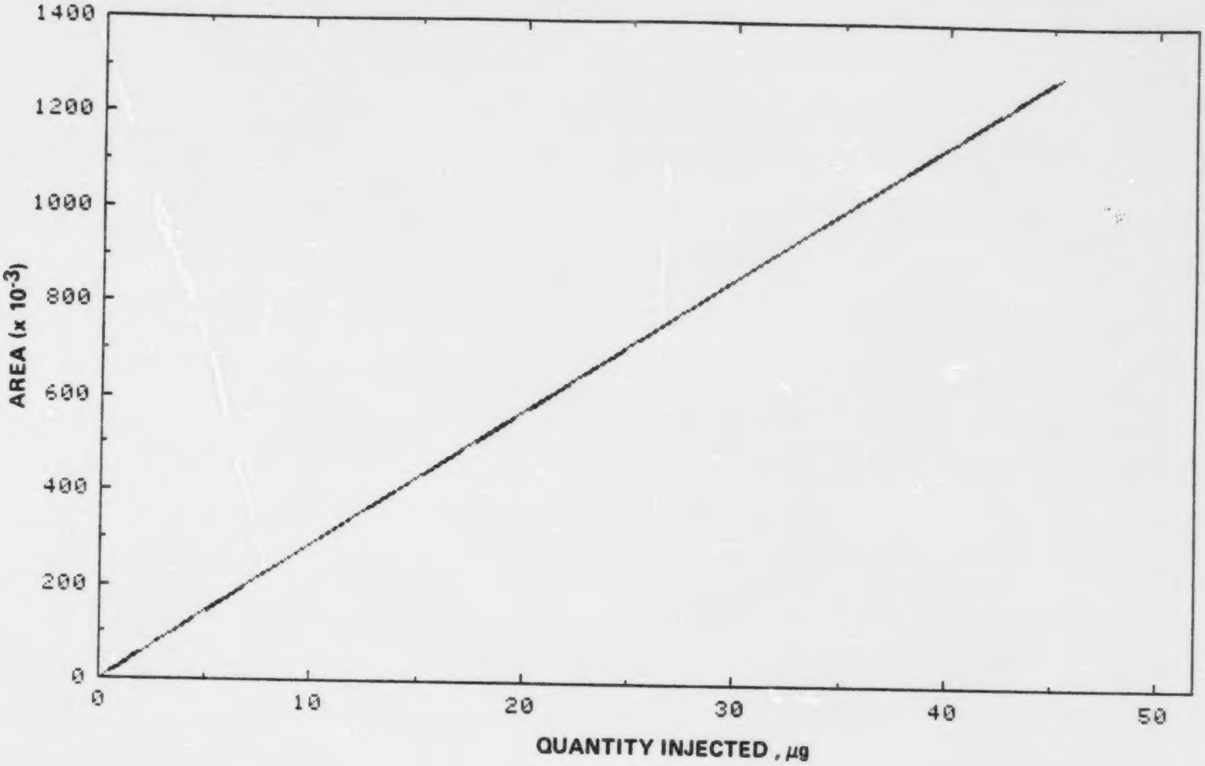

Figure C-62. Calibration curve for the determination of 2,4-dinitrophenol by HPLC/UV (254 nm).

Range: 0.18 - 45 μg
Correlation coefficient: 0.999
Slope: 2.86×10^1
y-Intercept: 1.22

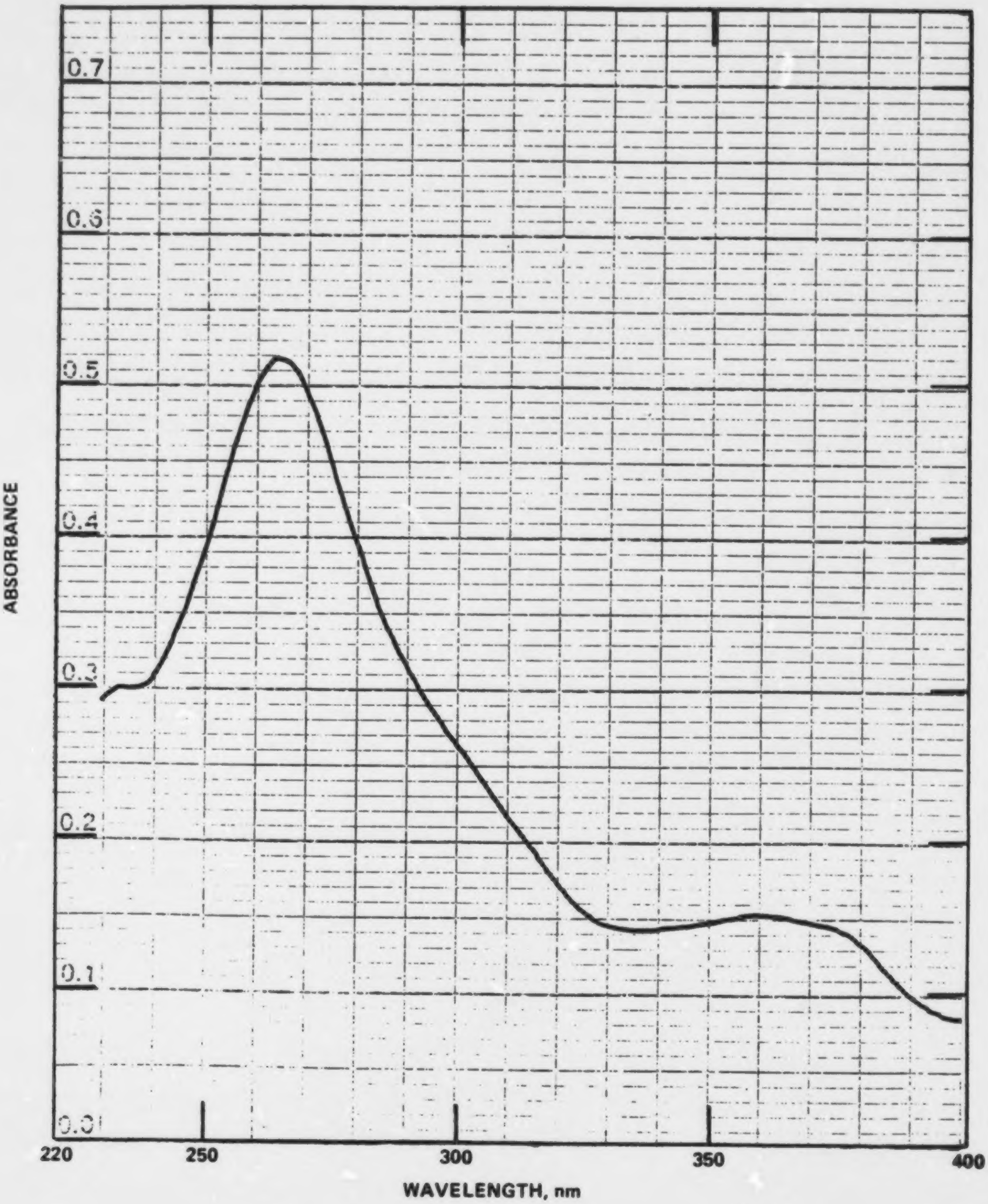

Figure C-63. UV spectrum for 4,6-dinitro-o-cresol.

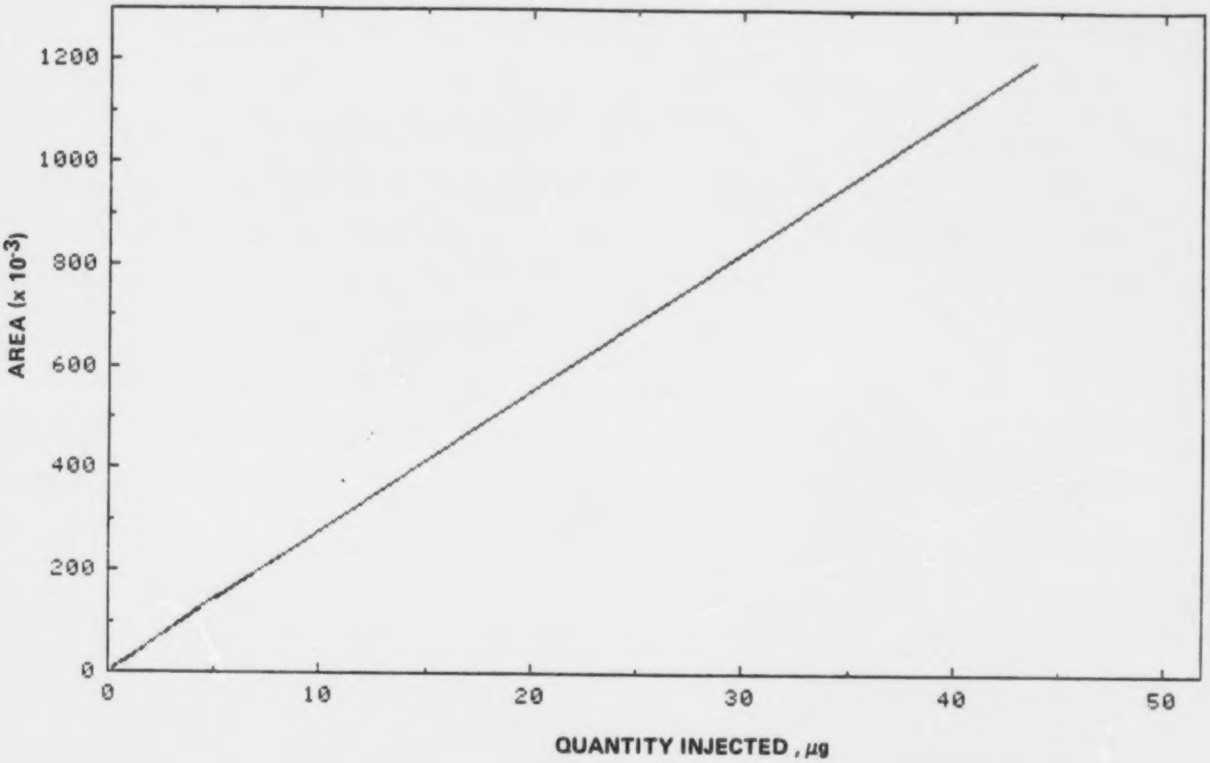

Figure C-64. Calibration curve for the determination of 4,6-dinitro-o-cresol by HPLC/UV (254 nm).

Range: 0.18 - 44 µg
Correlation coefficient: 0.999
Slope: 2.74×10^1
y-Intercept: 1.92

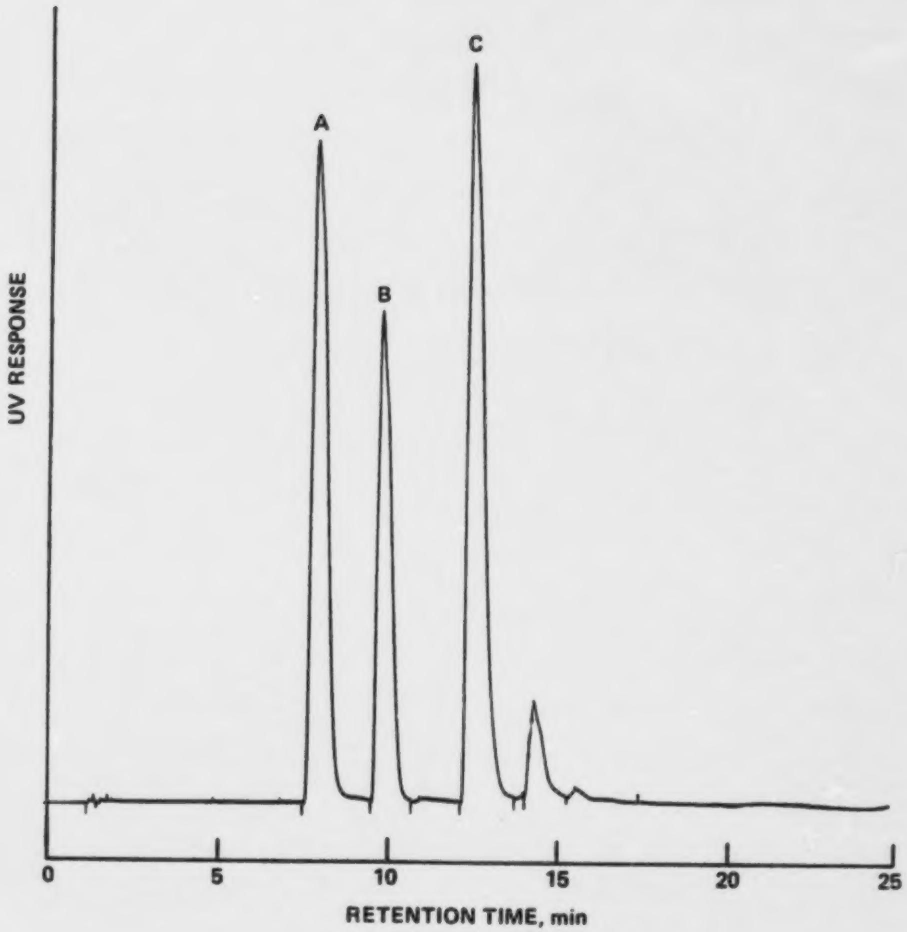

Figure C-65. Chromatogram by HPLC/UV (254 nm) for

(A) benzidine(t_R = 8.1 min),
(B) 3,3'-dimethylbenzidine(t_R = 10.0 min), and
(C) 4,4'-methylenebis(2-chloroaniline)(t_R = 12.7 min).

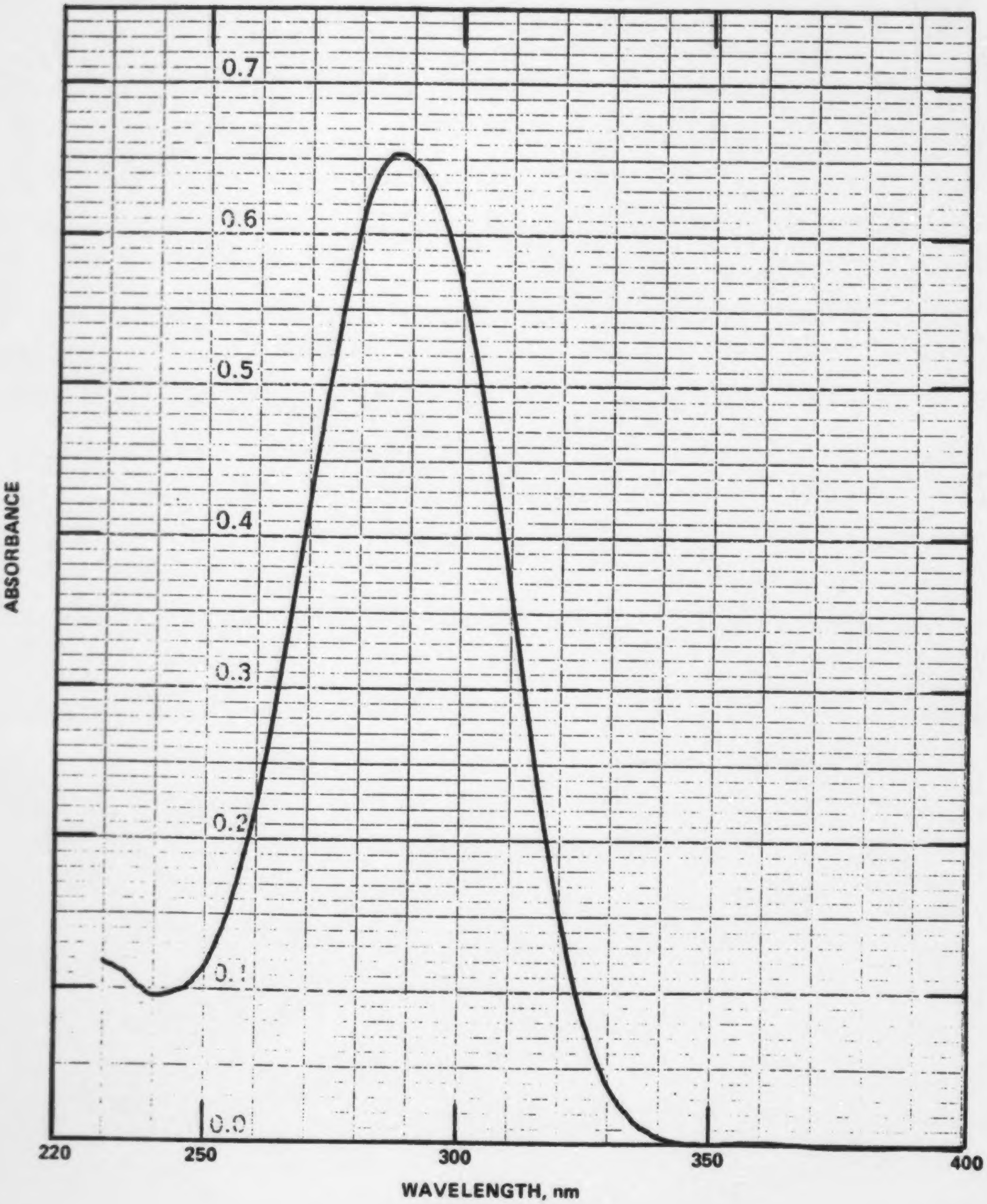

Figure C-66. UV spectrum for benzidine.

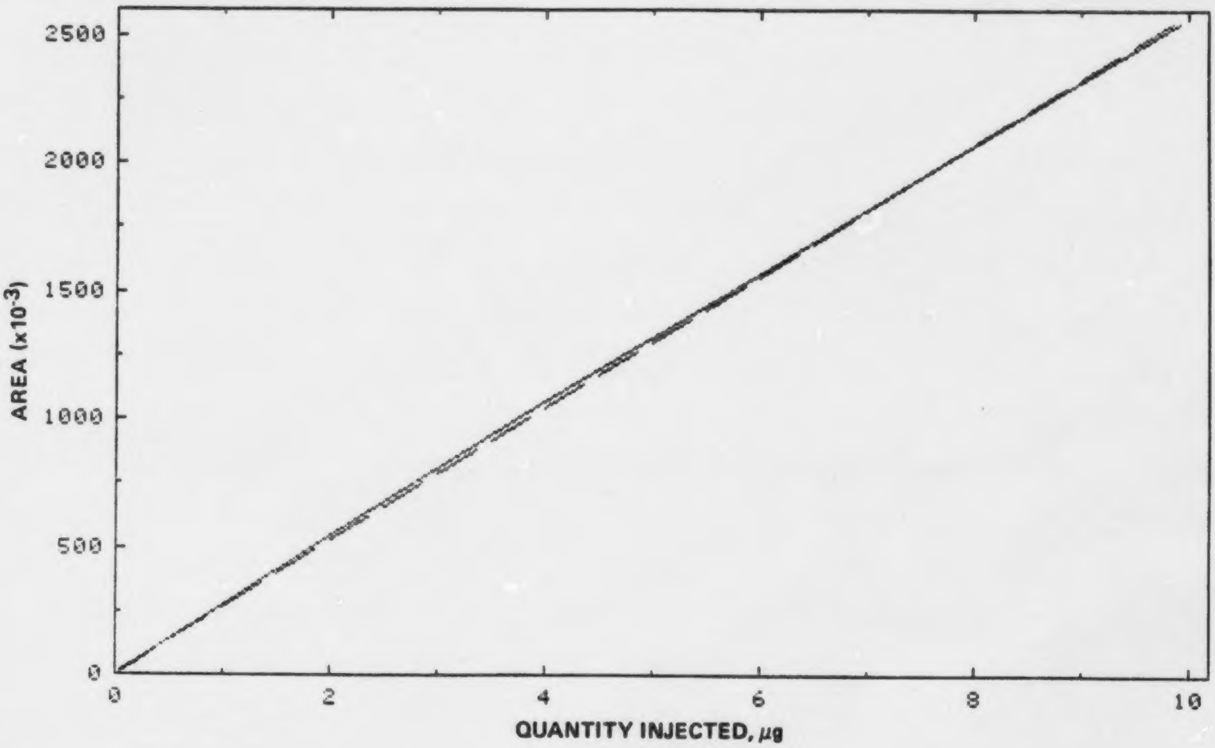

Figure C-67. Calibration curve for the determination of benzidine by HPLC/UV (254 nm).

Range: 0.099 - 9.9 µg
Correlation coefficient: 0.999
Slope: 2.57×10^2
y-Intercept: 1.09×10^1

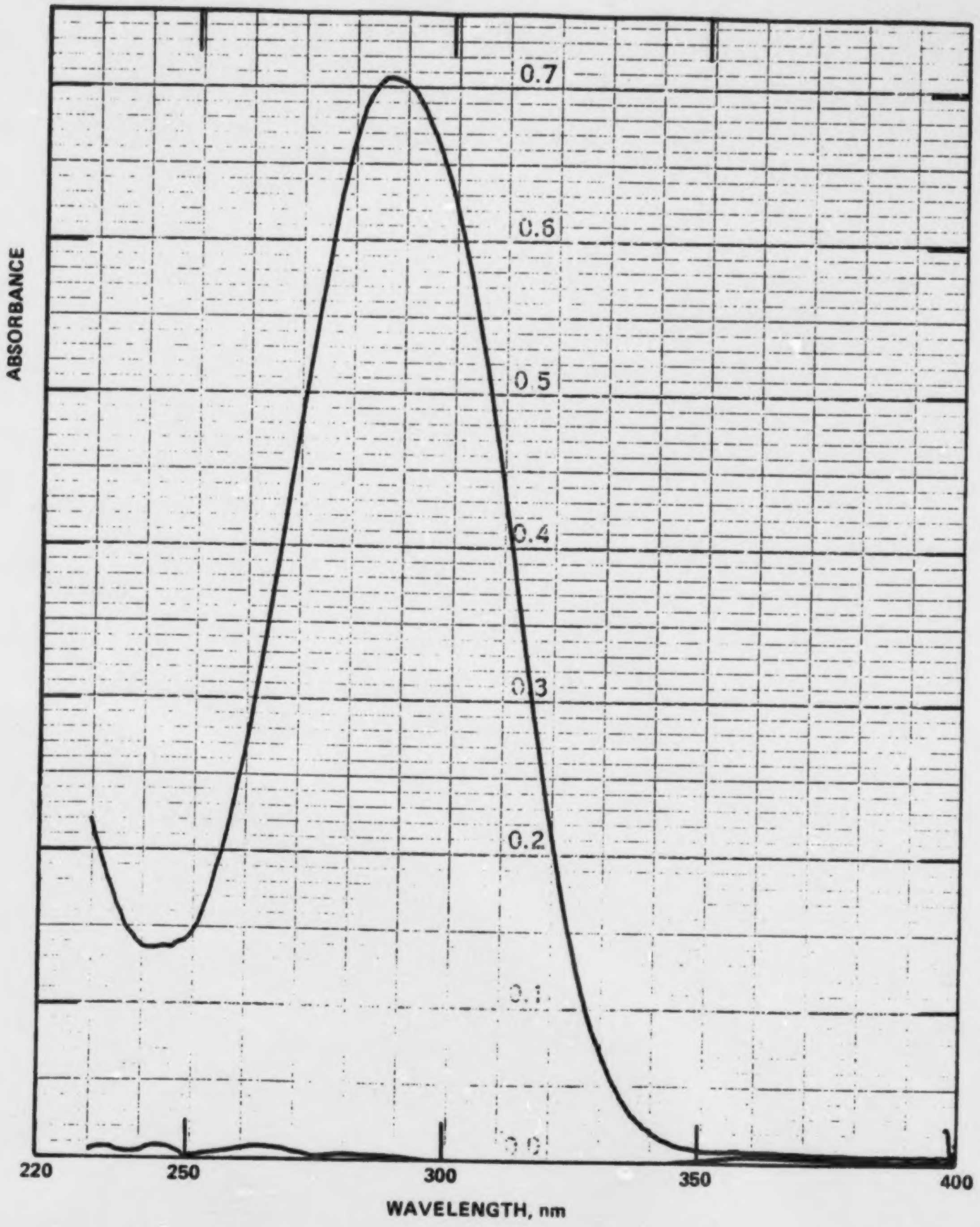

Figure C-68. UV spectrum for 3,3'-dimethylbenzidine.

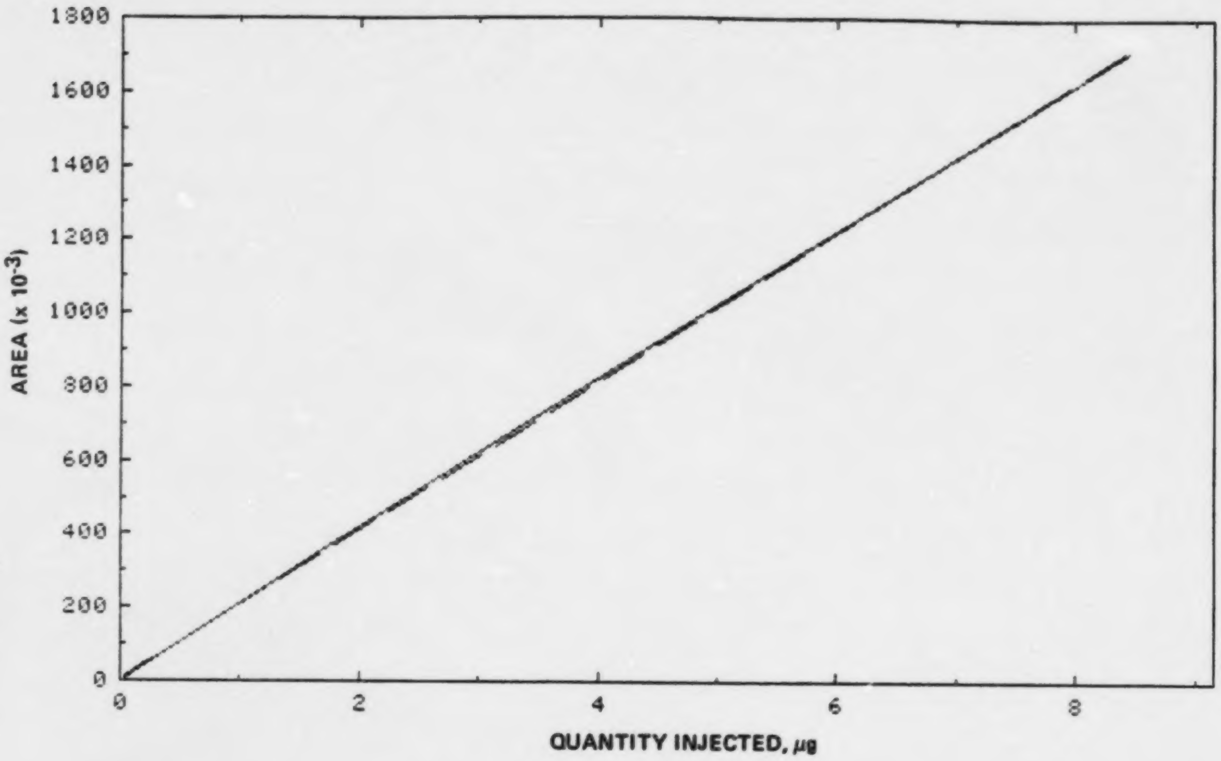

Figure C-69. Calibration curve for the determination of 3,3'-dimethylbenzidine by HPLC/UV (254 nm).

Range: 0.084 - 8.4 µg
Correlation coefficient: 0.999
Slope: 2.03×10^2
y-Intercept: 4.56

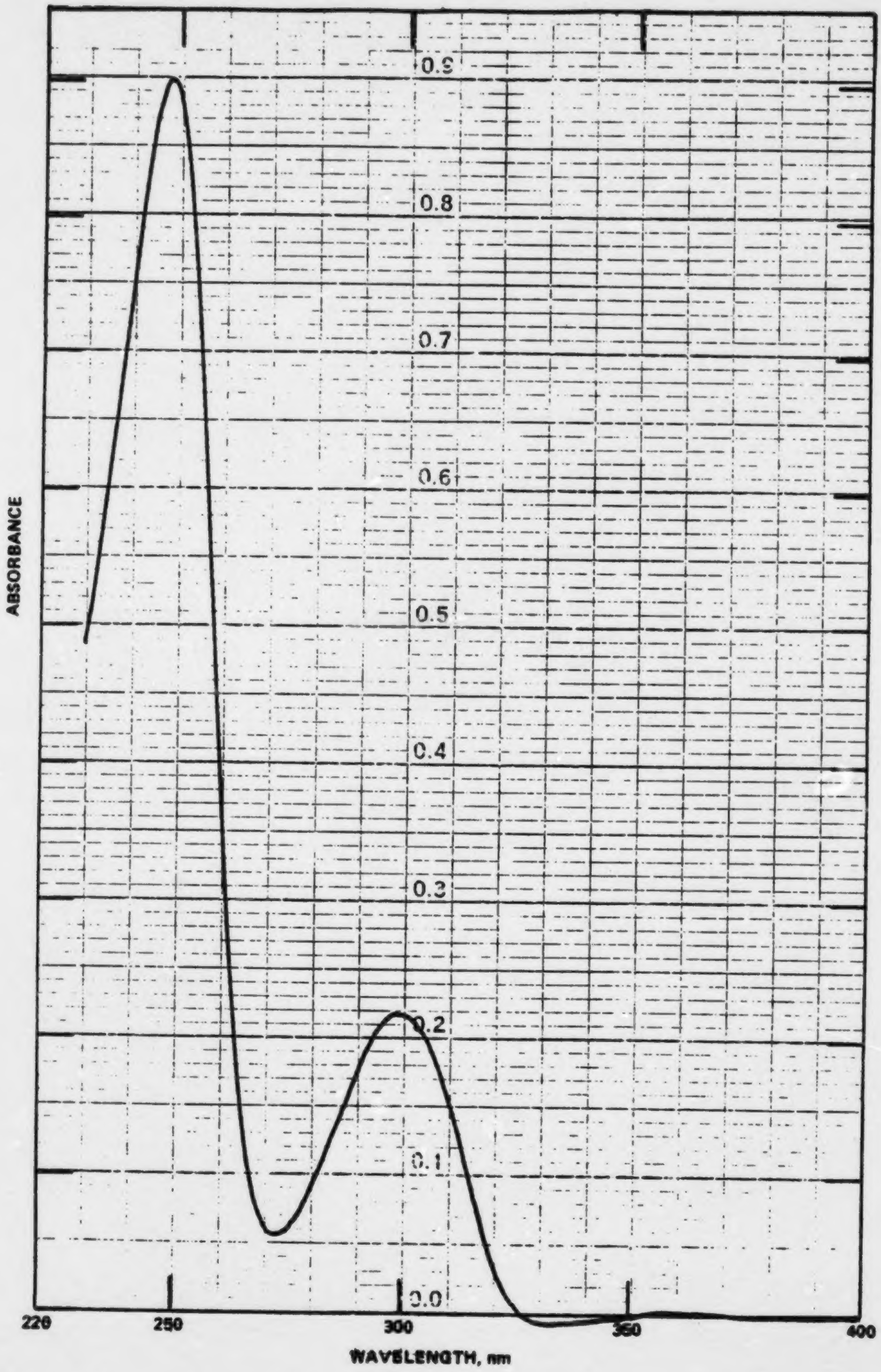

Figure C-70. UV spectrum for 4,4'-methylenebis(2-chloroaniline).

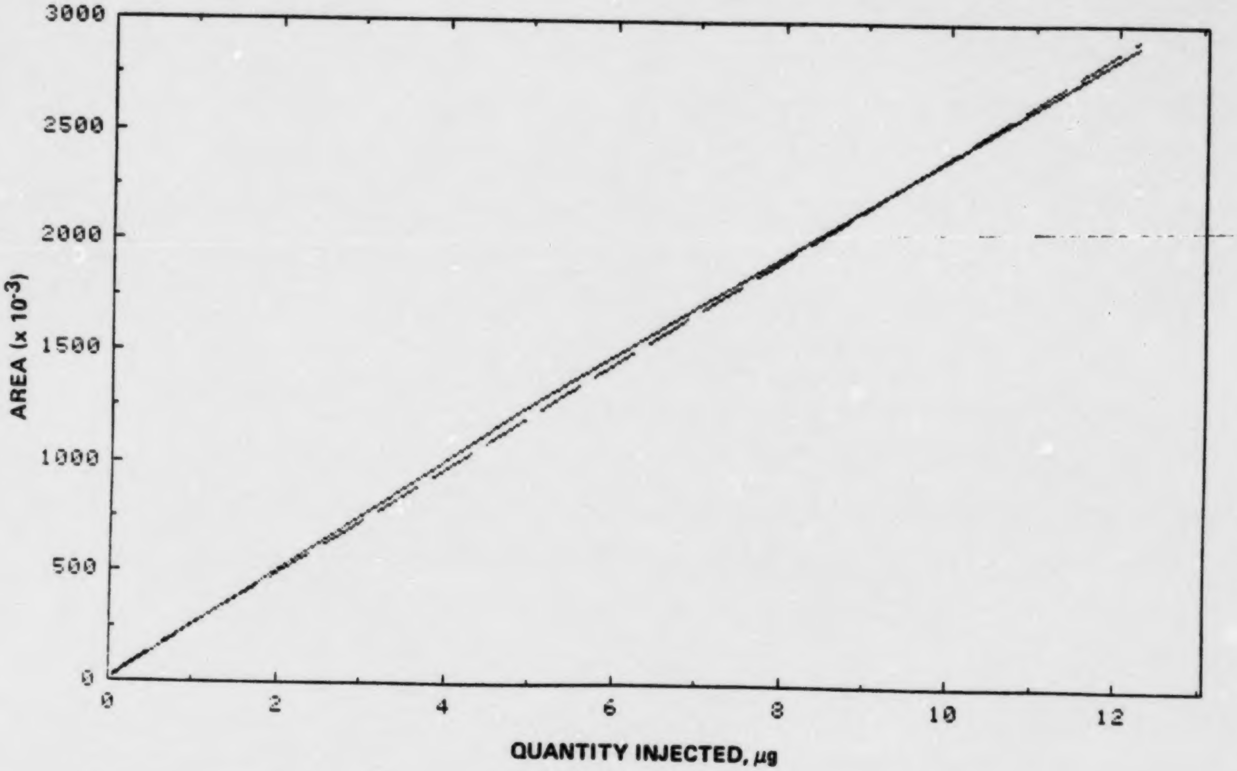

Figure C-71. Calibration curve for the determination of 4,4'-methylenebis(2-chloroaniline) by HPLC/UV (254 nm).

Range: 0.24 - 12 µg
Correlation coefficient: 0.999
Slope: 2.37×10^2
y-Intercept: 2.13×10^1

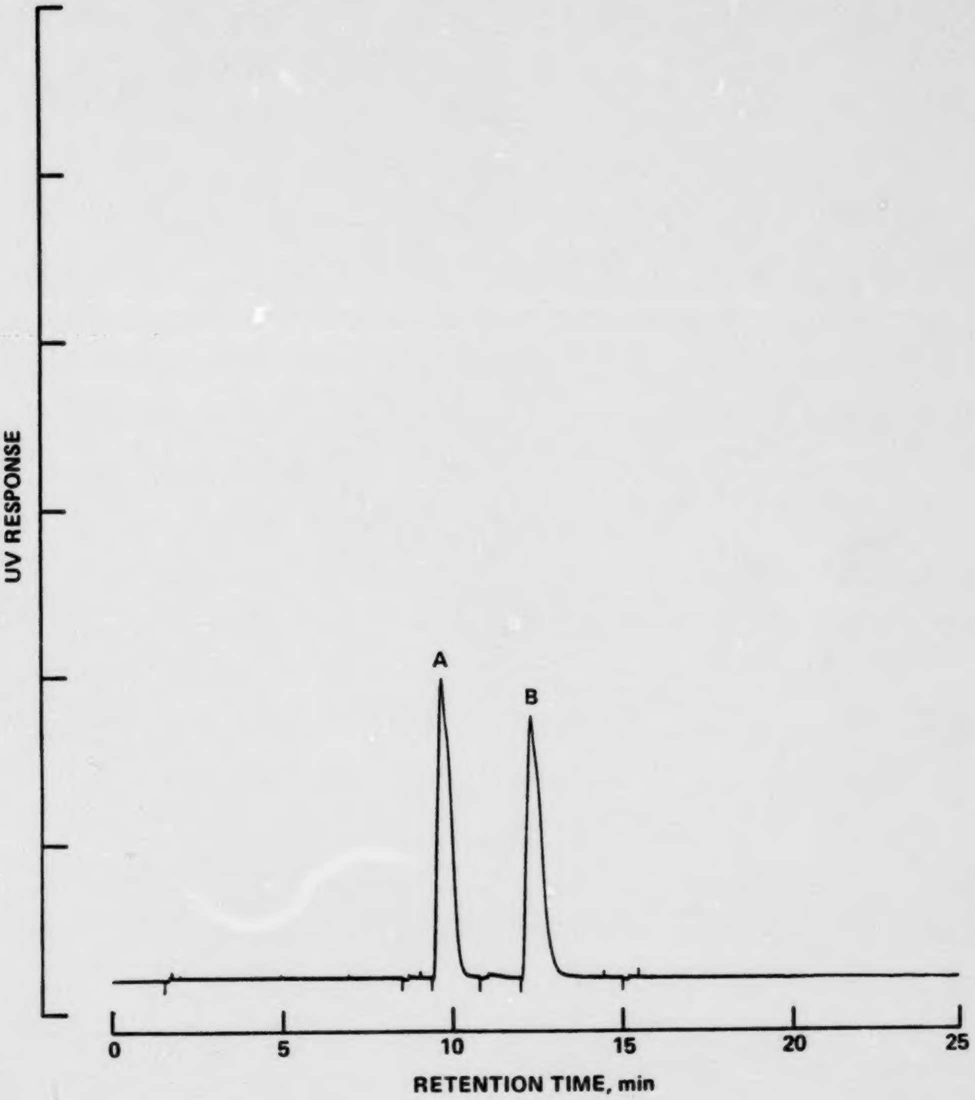

Figure C-72. Chromatogram by HPLC/UV (254 nm) for

(A) 3,3'-dimethoxybenzidine(t_R = 9.8 min) and
(B) 3,3'-dichlorobenzidine(t_R = 12.5 min).

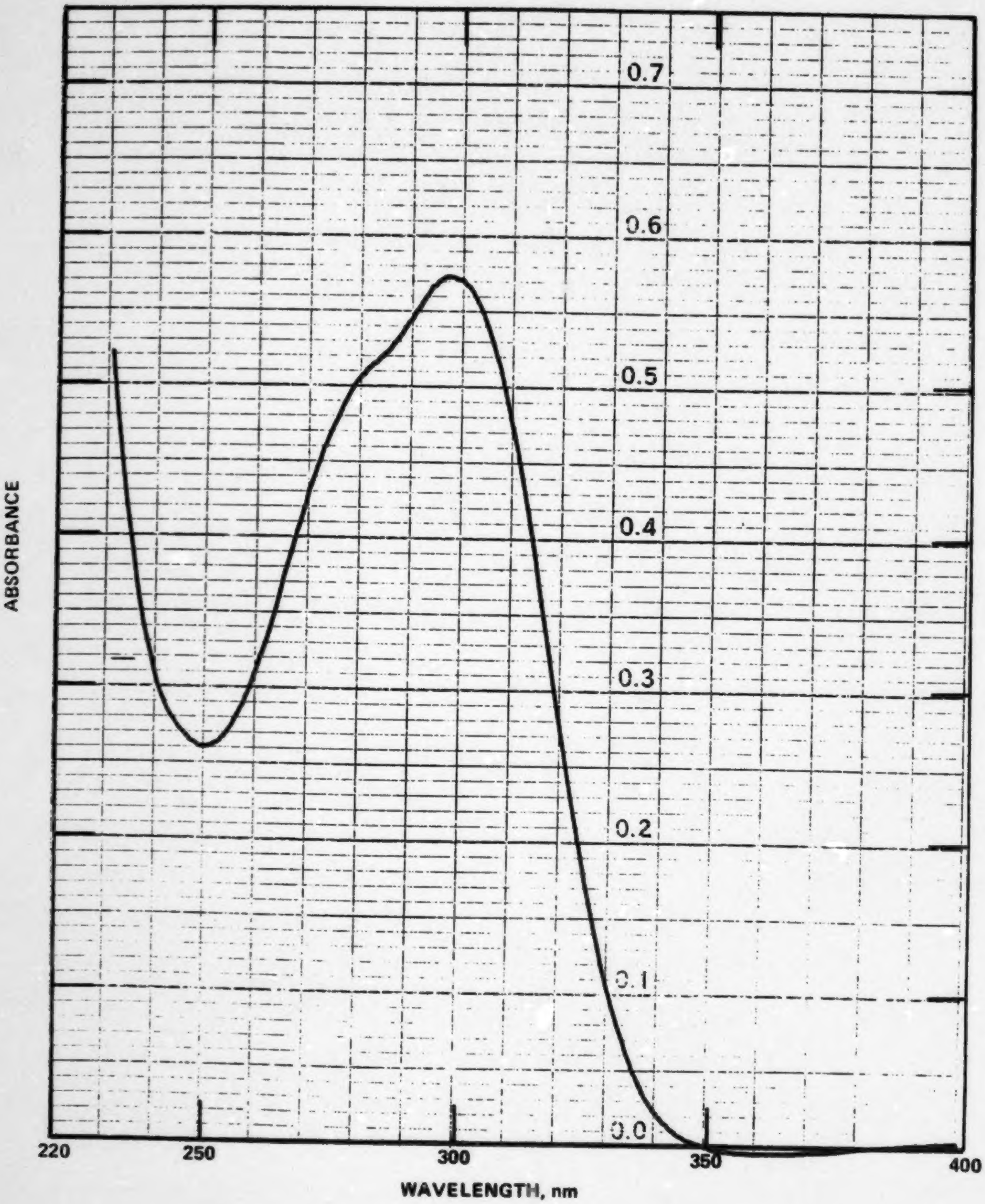

Figure C-73. UV spectrum for 3,3'-dimethoxybenzidine.

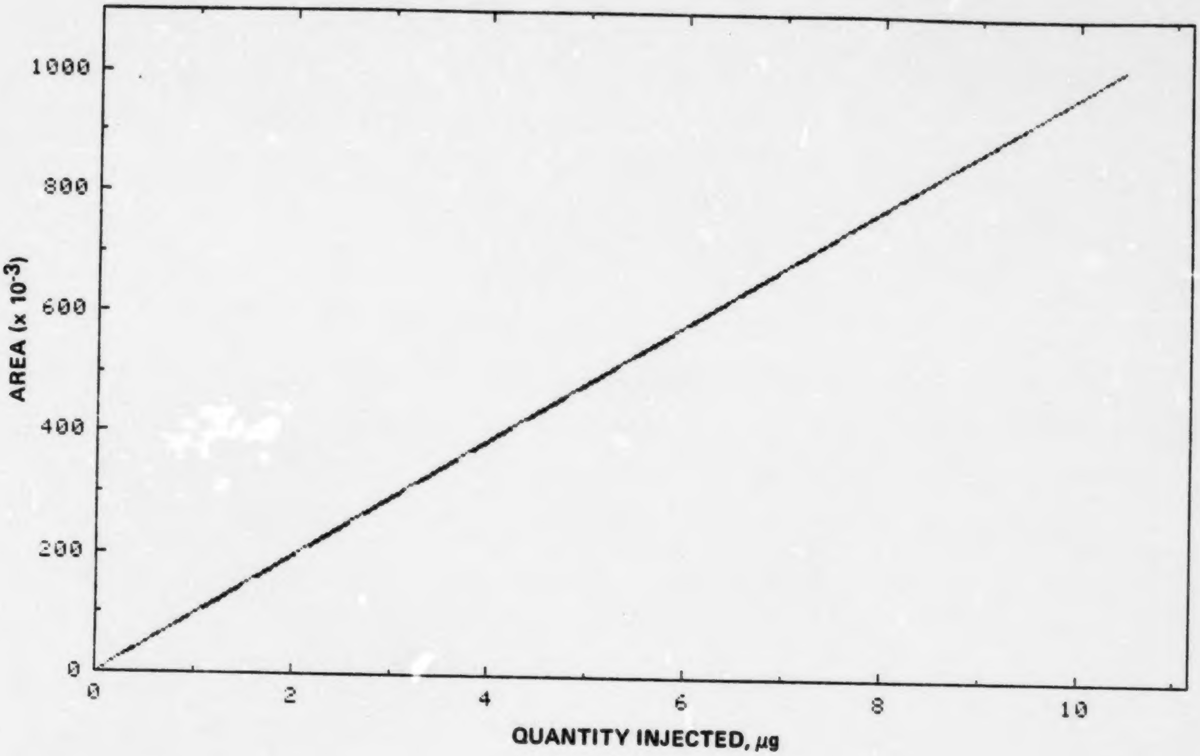

Figure C-74. Calibration curve for the determination of 3,3'-dimethoxybenzidine by HPLC/UV (254 nm).

Range: 0.041 - 10 µg
Correlation coefficient: 0.999
Slope: 9.70×10^1
y-Intercept: 1.19

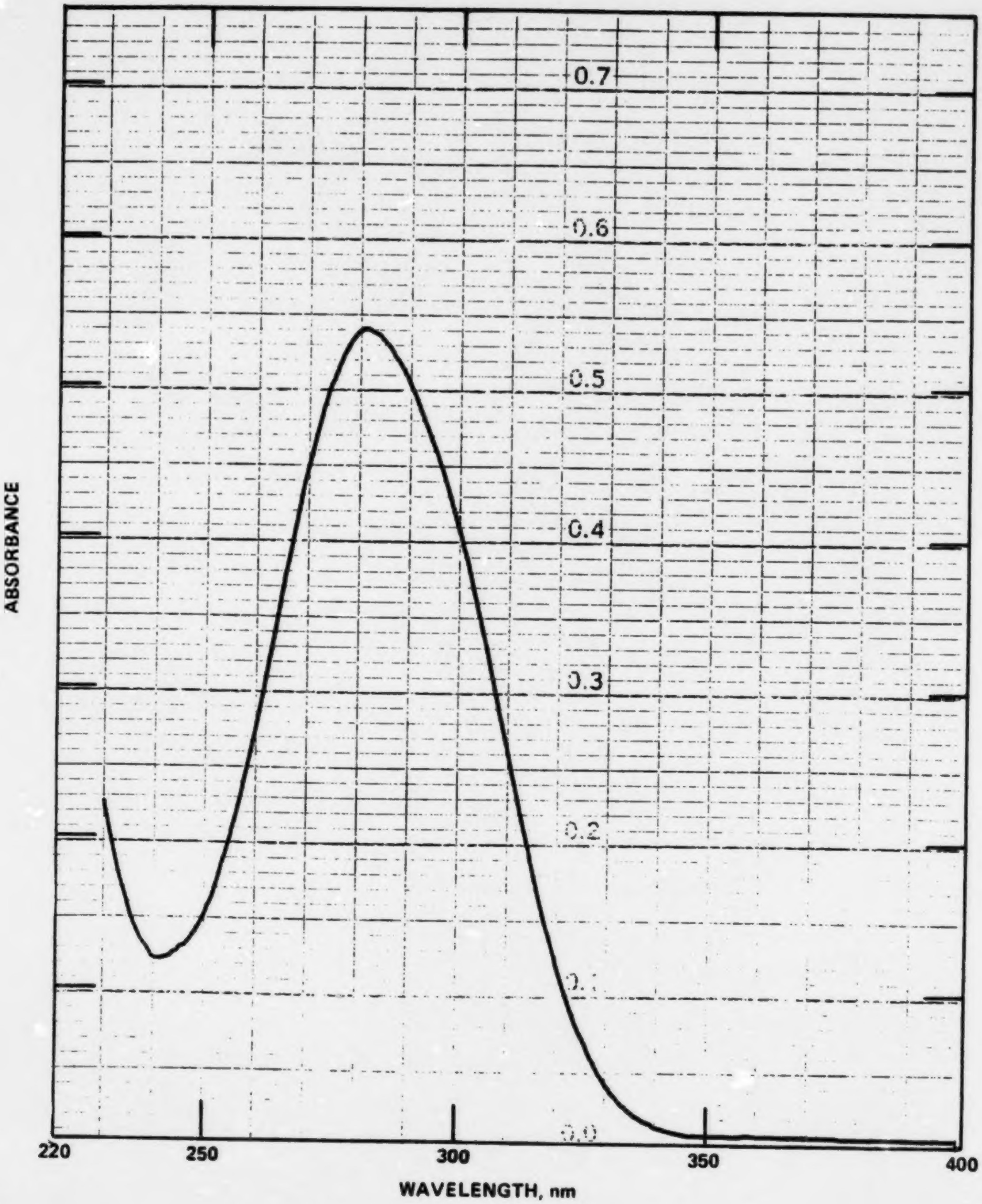

Figure C-75. UV spectrum for 3,3'-dichlorobenzidine.

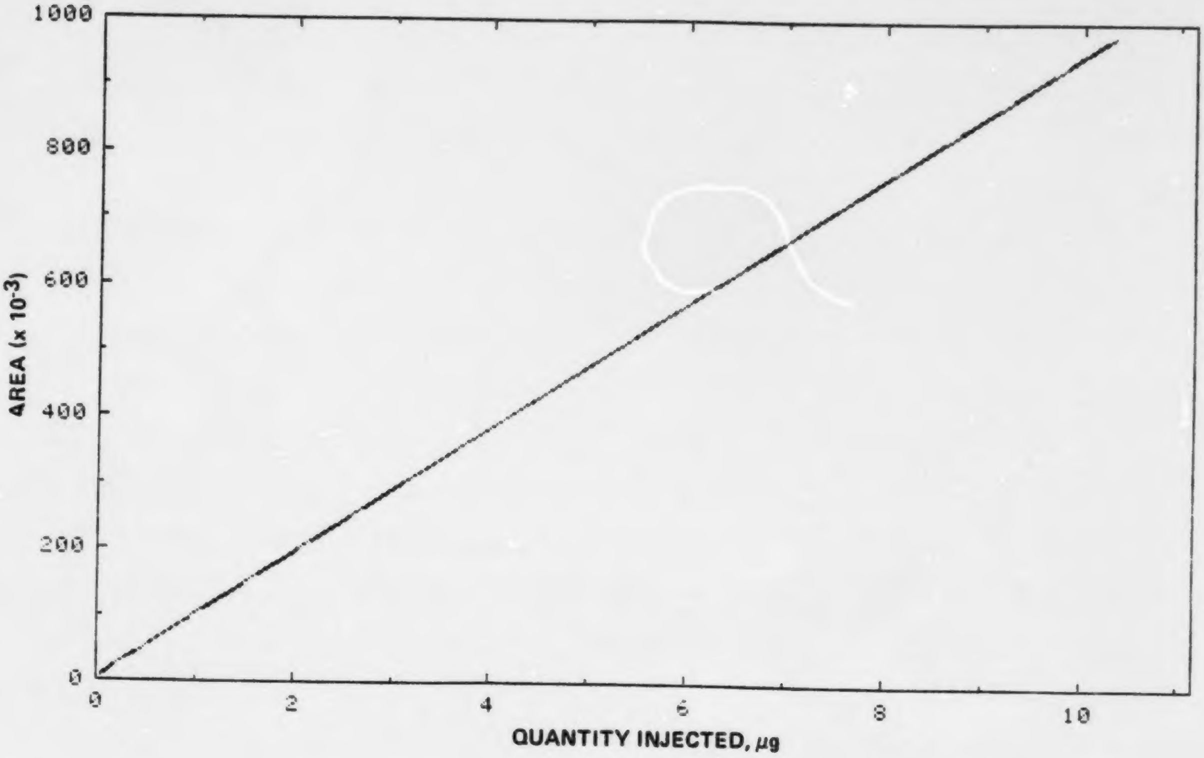

Figure C-76. Calibration curve for the determination of 3,3'-dichlorobenzidine by HPLC/UV (254 nm).

Range: 0.041 - 10 μg
Correlation coefficient: 0.999
Slope: 9.45×10^1
y-Intercept: 5.62

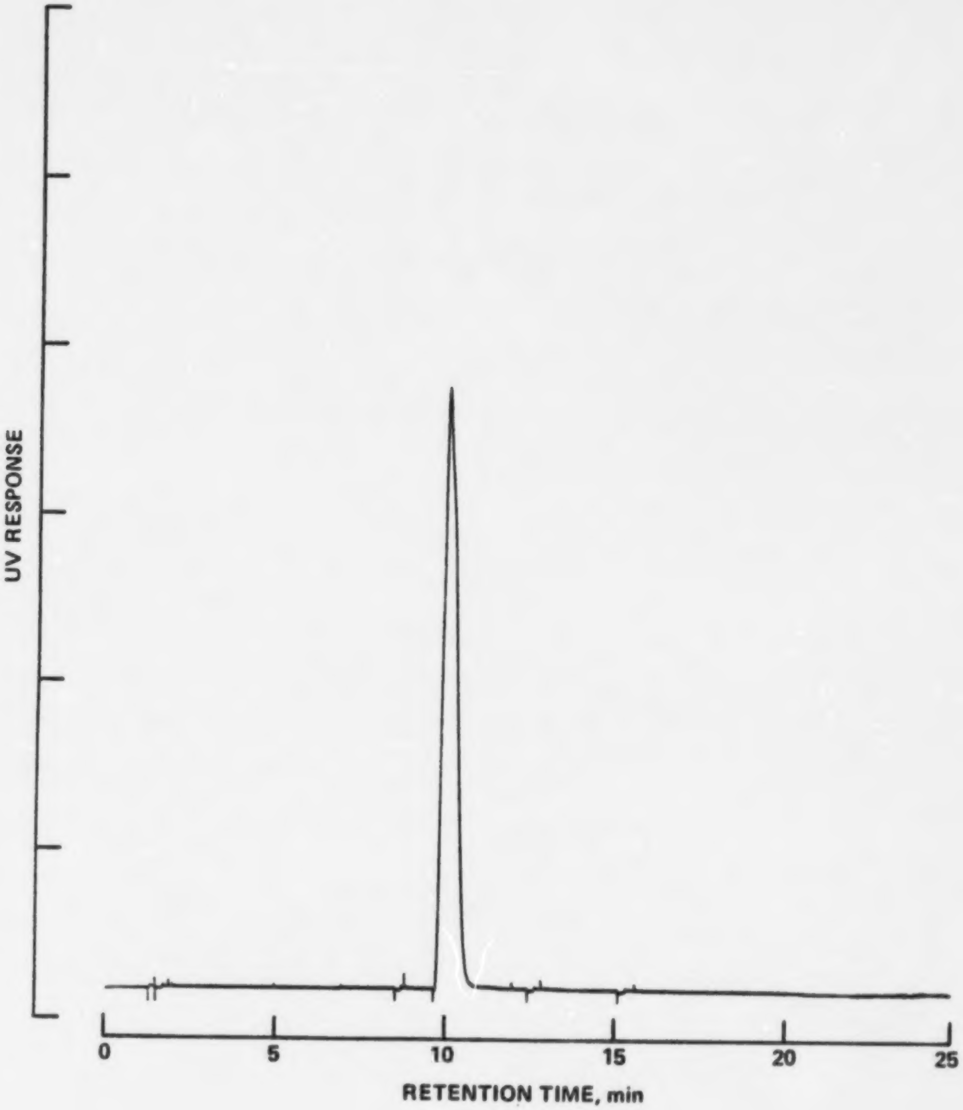

Figure C-77. Chromatogram by HPLC/UV (254 nm) for o-toluidine.

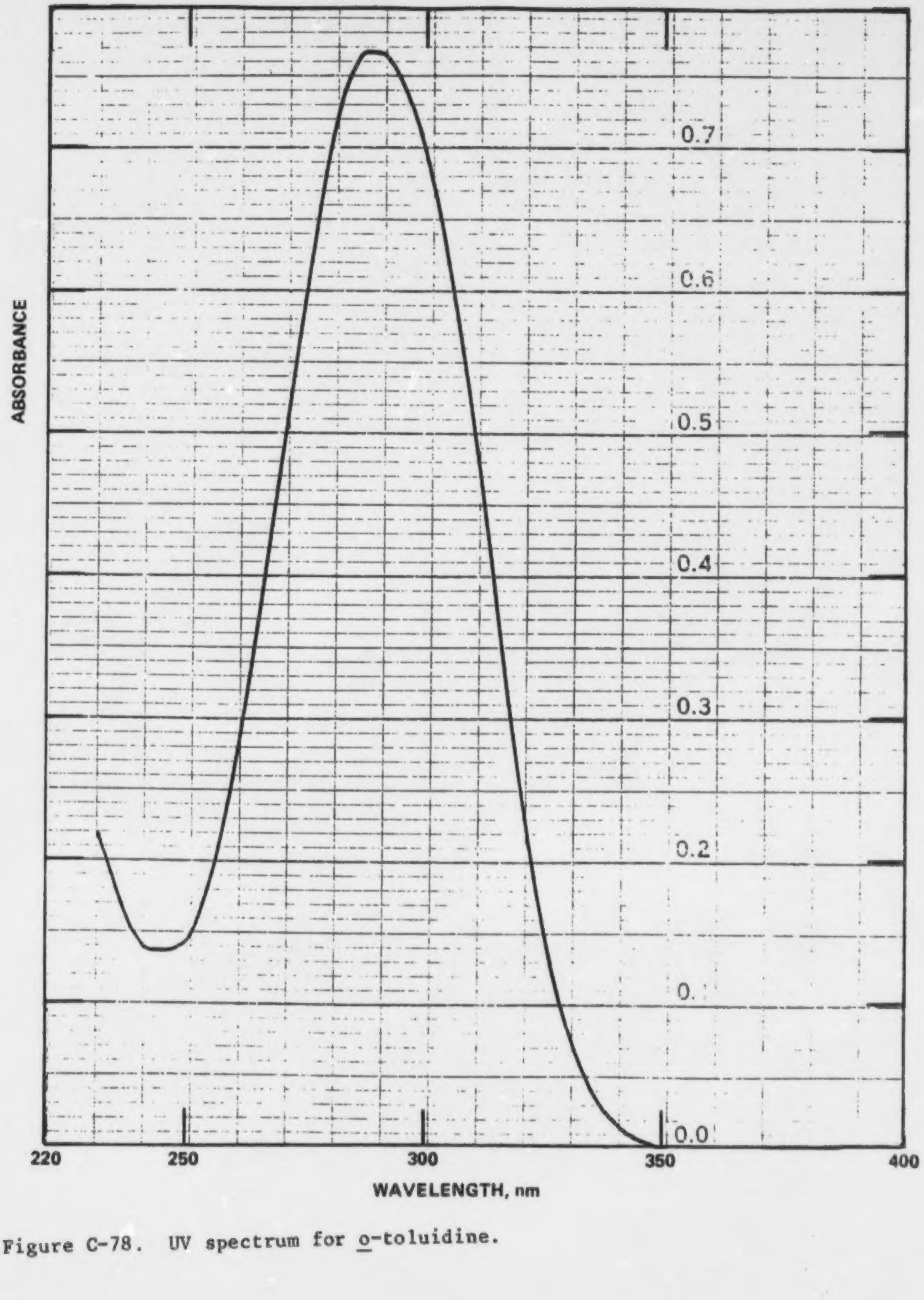

Figure C-78. UV spectrum for o-toluidine.

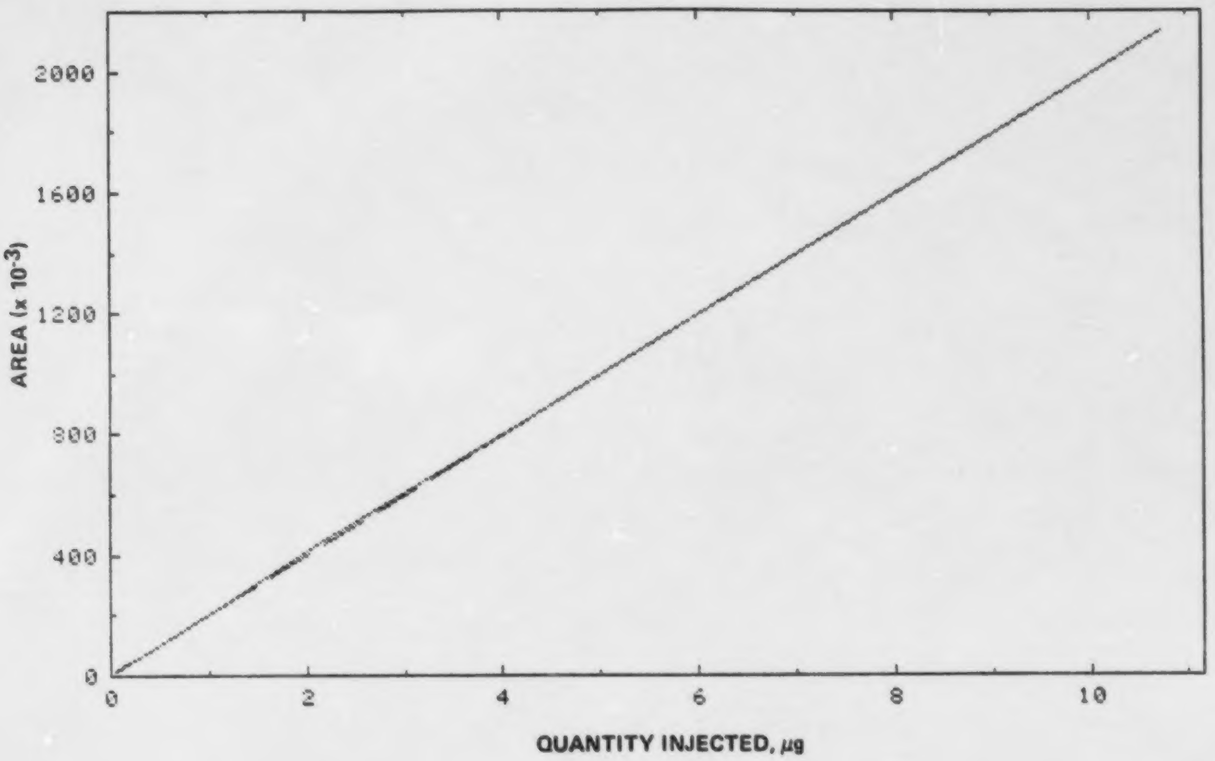

Figure C-79. Calibration curve for the determination of *o*-toluidine by HPLC/UV (254 nm).

Range: 0.043 - 11 µg
Correlation coefficient: 0.999
Slope: 1.98 x 10^2
y-Intercept: 4.24

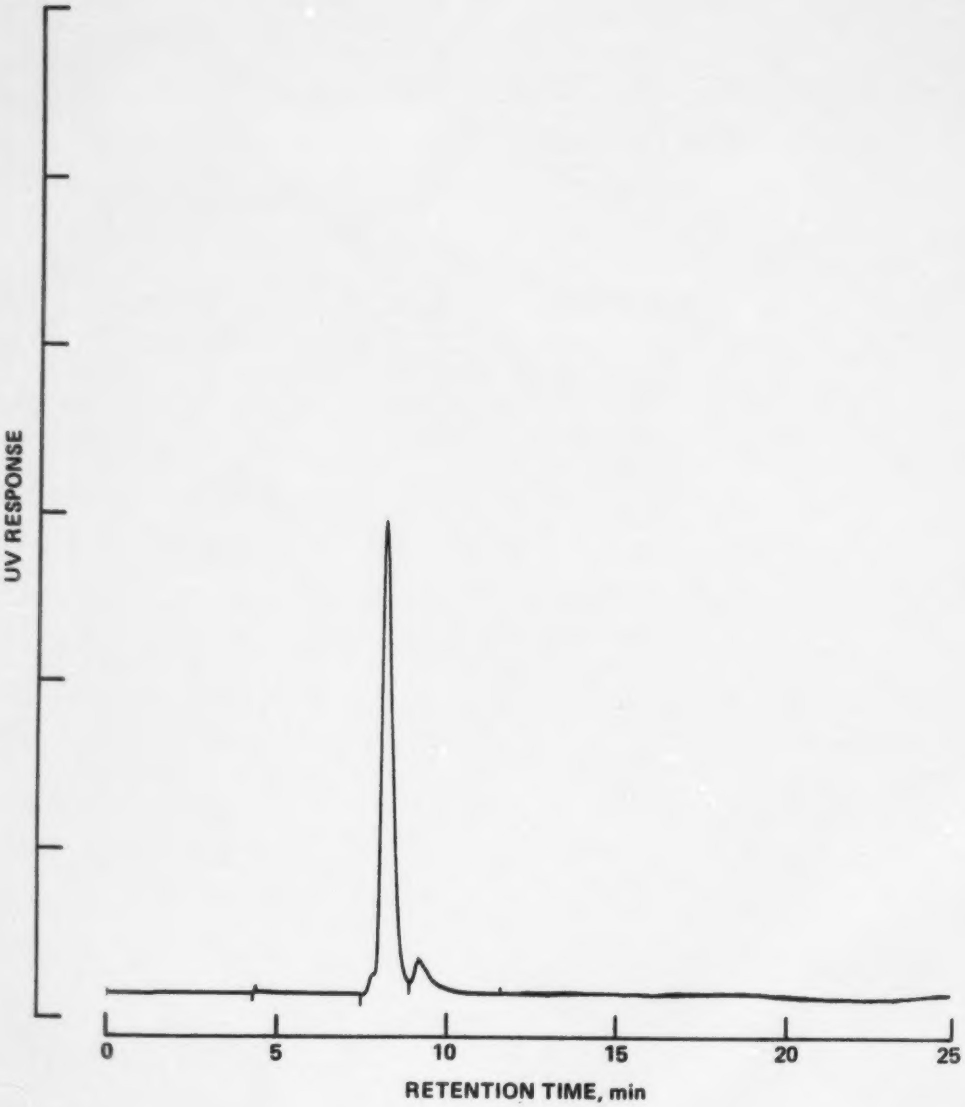

Figure C-80. Chromatogram by HPLC/VIS (588 nm) for Trypan Blue.

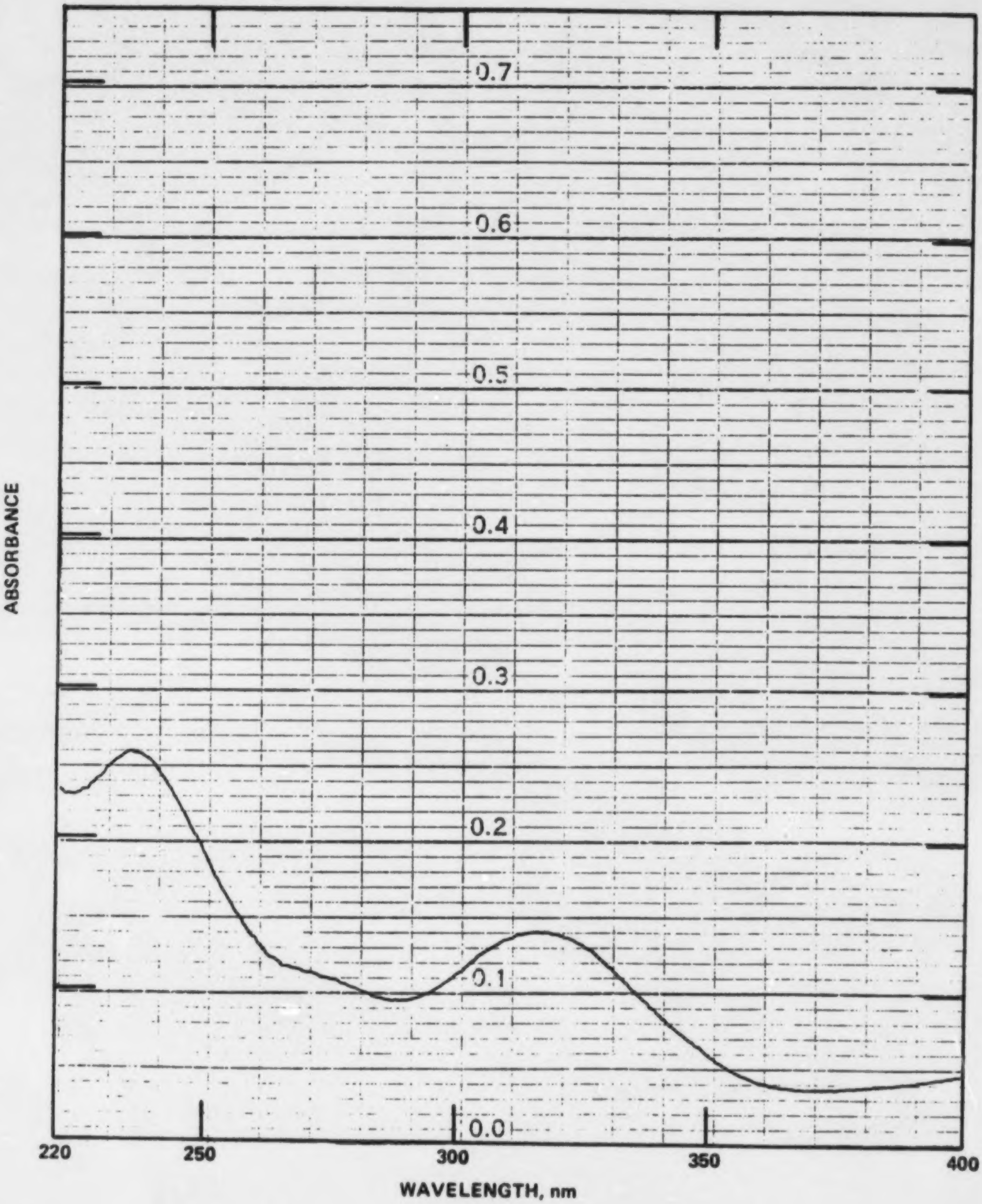

Figure C-81. UV spectrum for Trypan Blue.

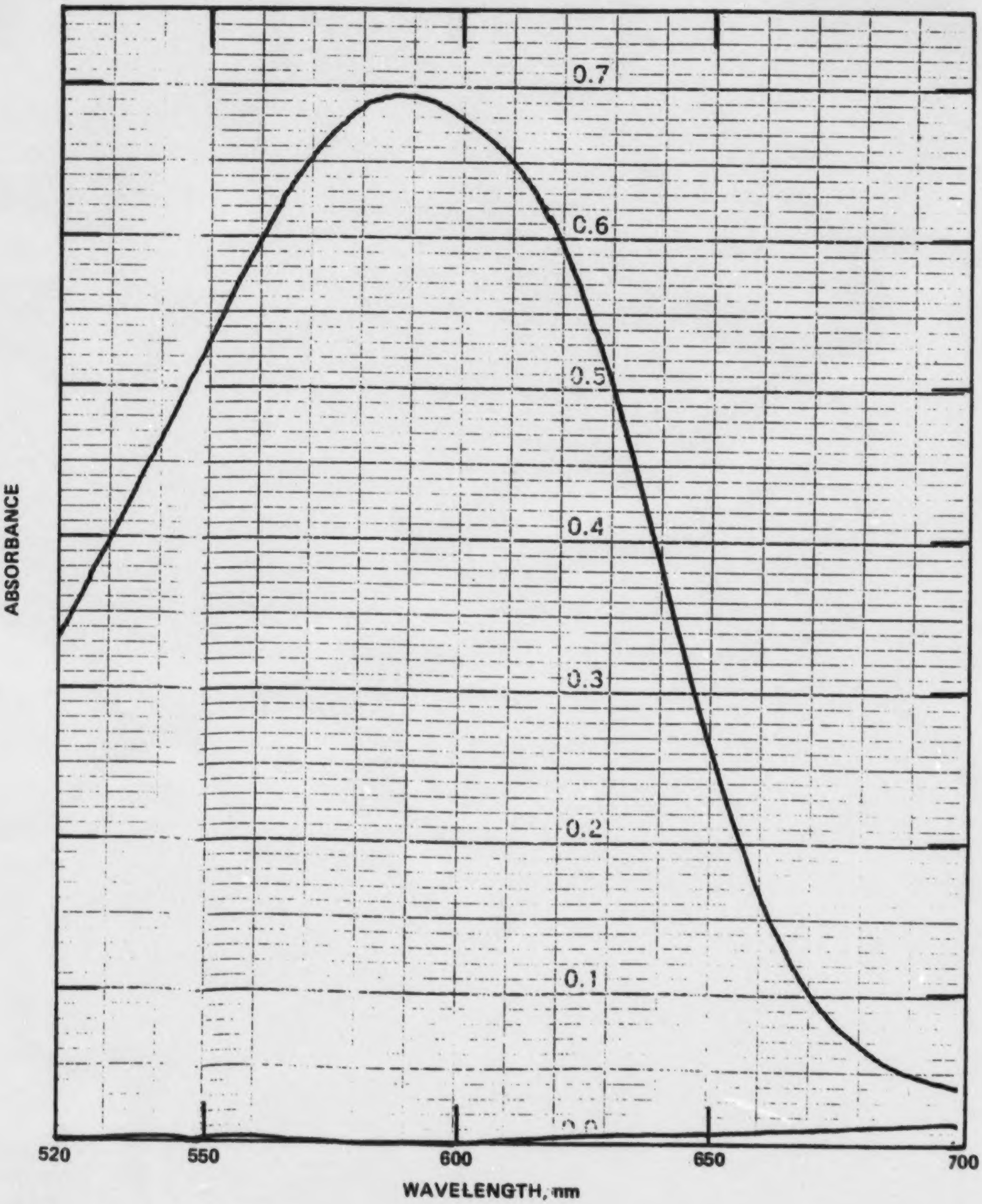

Figure C-82. Visible spectrum for Trypan Blue.

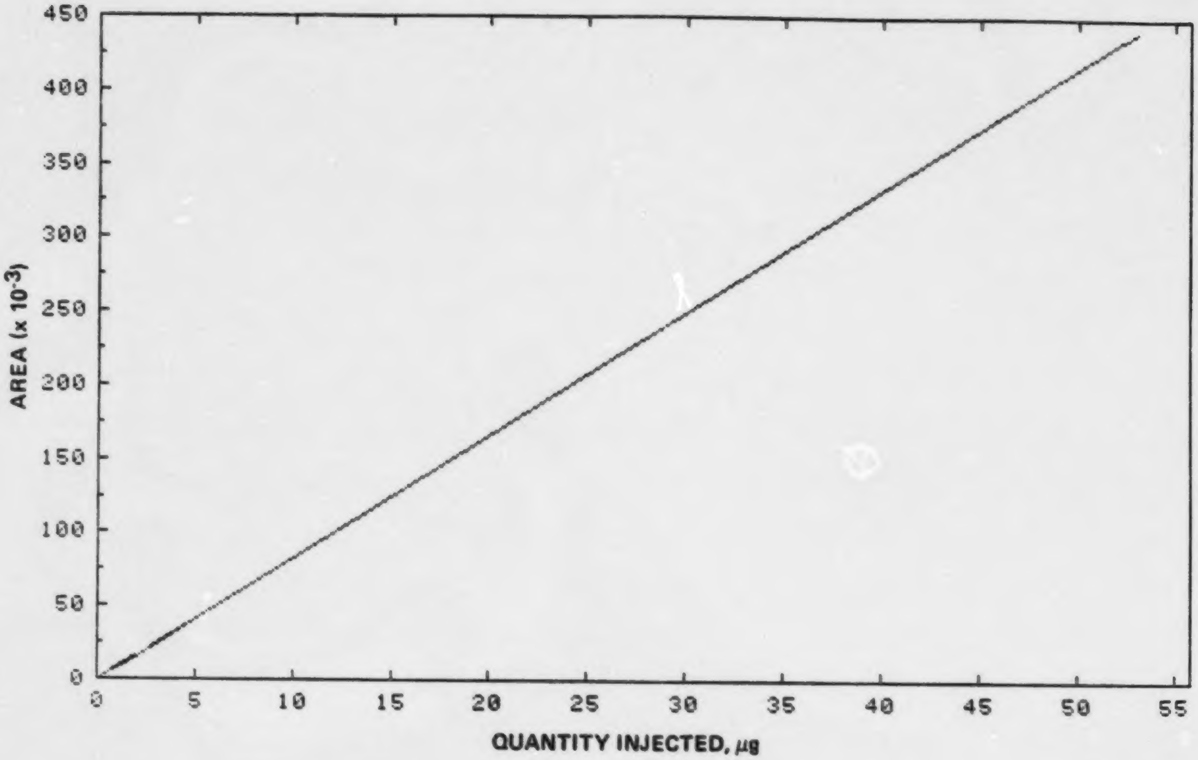

Figure C-83. Calibration curve for the determination of Trypan Blue by HPLC/UV (588 nm).

Range: 0.53 - 53 μg
Correlation coefficient: 0.999
Slope: 8.32 x 10
y-Intercept: -5.35×10^{-1}

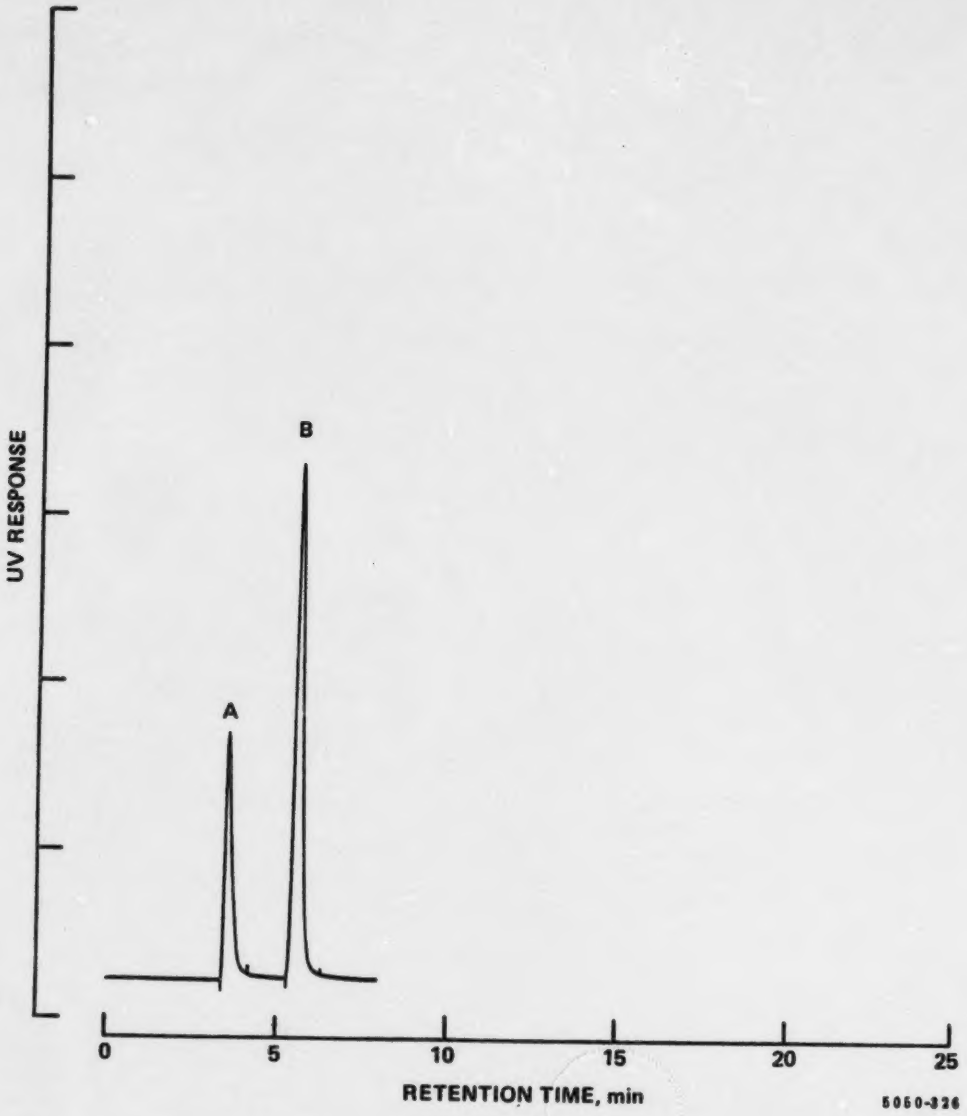

Figure C-84. Chromatogram by HPLC/UV (254 nm) for

(A) thiourea(t_R = 3.5 min) and
(B) 1-acetyl-2-thiourea(t_R = 5.6 min).

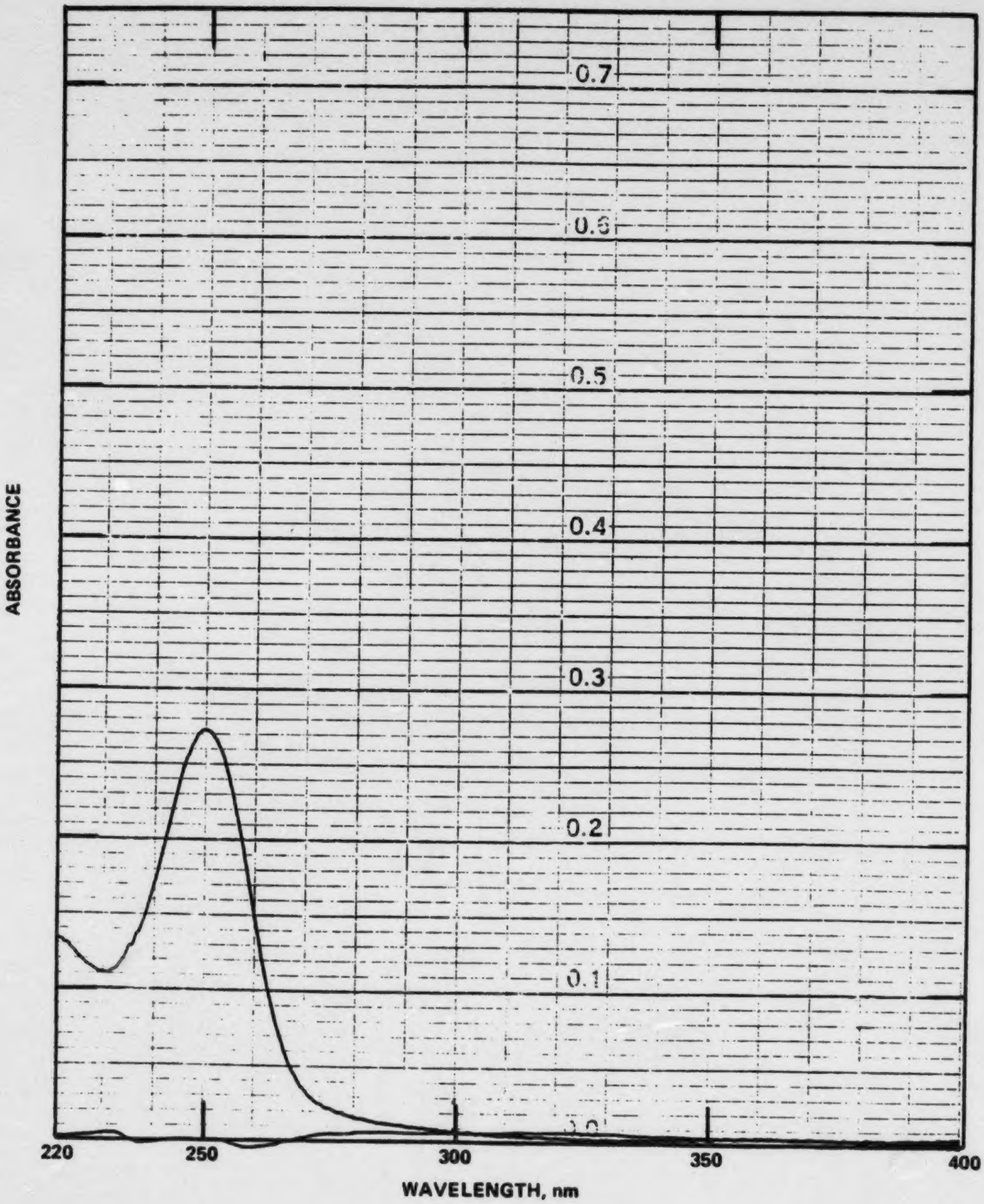

Figure C-85. UV spectrum for thiourea.

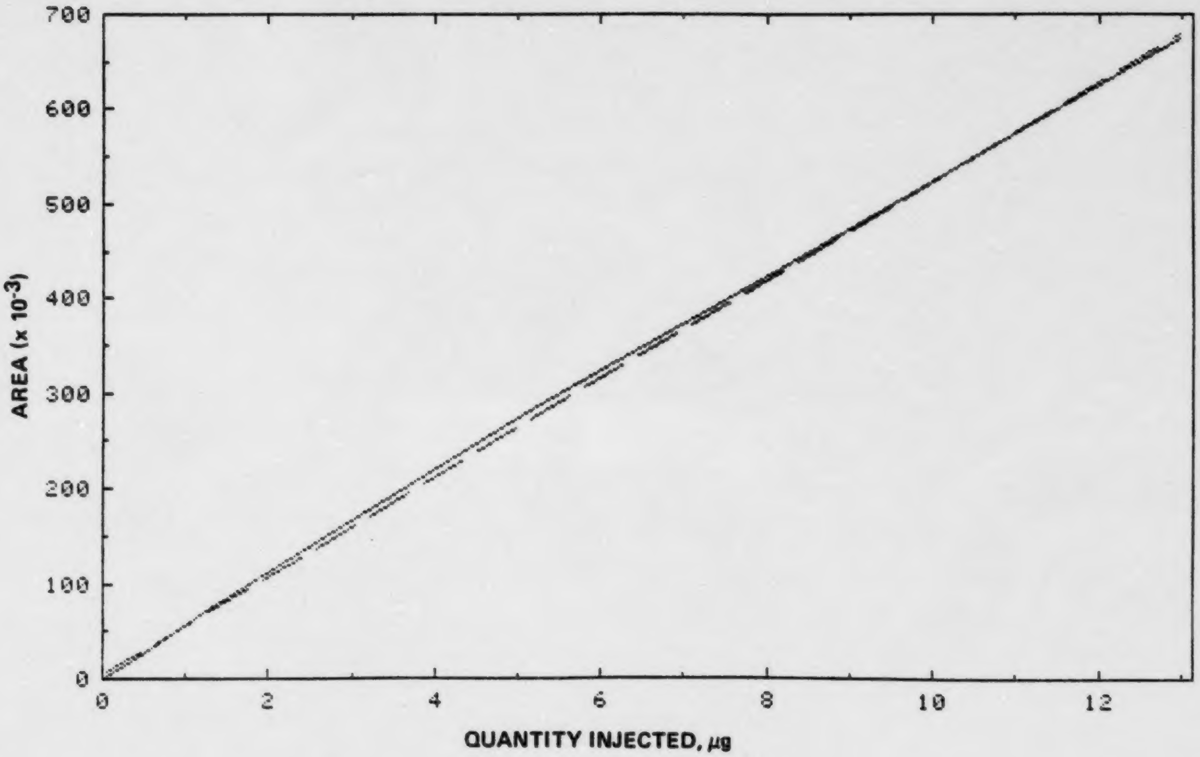

Figure C-86. Calibration curve for the determination of thiourea by HPLC/UV (254 nm).

Range: 0.26 - 13 µg
Correlation coefficient: 0.999
Slope: 5.20×10^{1}
y-Intercept: 3.89

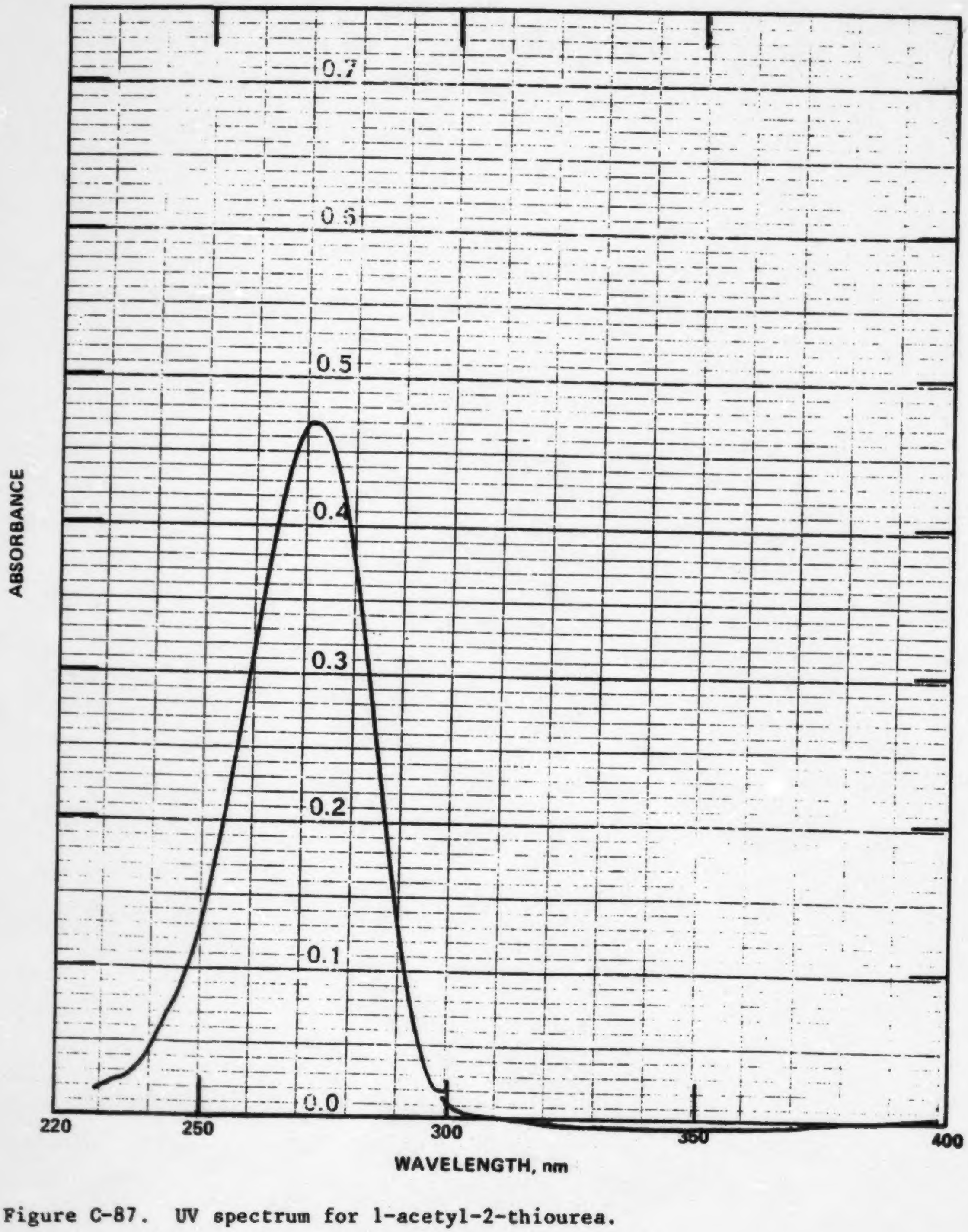

Figure C-87. UV spectrum for 1-acetyl-2-thiourea.

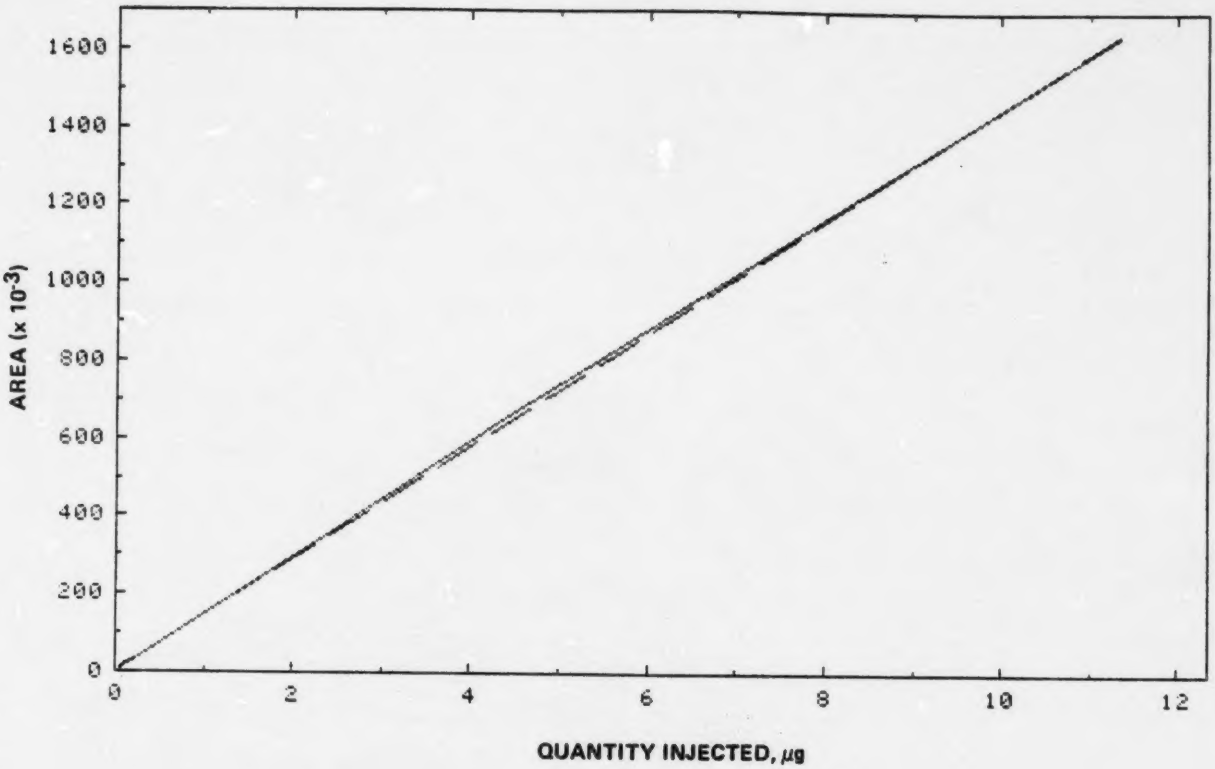

Figure C-88. Calibration curve for the determination of 1-acetyl-2-thiourea by HPLC/UV (254 nm).

Range: 0.11 - 11 µg
Correlation coefficient: 0.999
Slope: 1.45×10^2
y-Intercept: 3.54

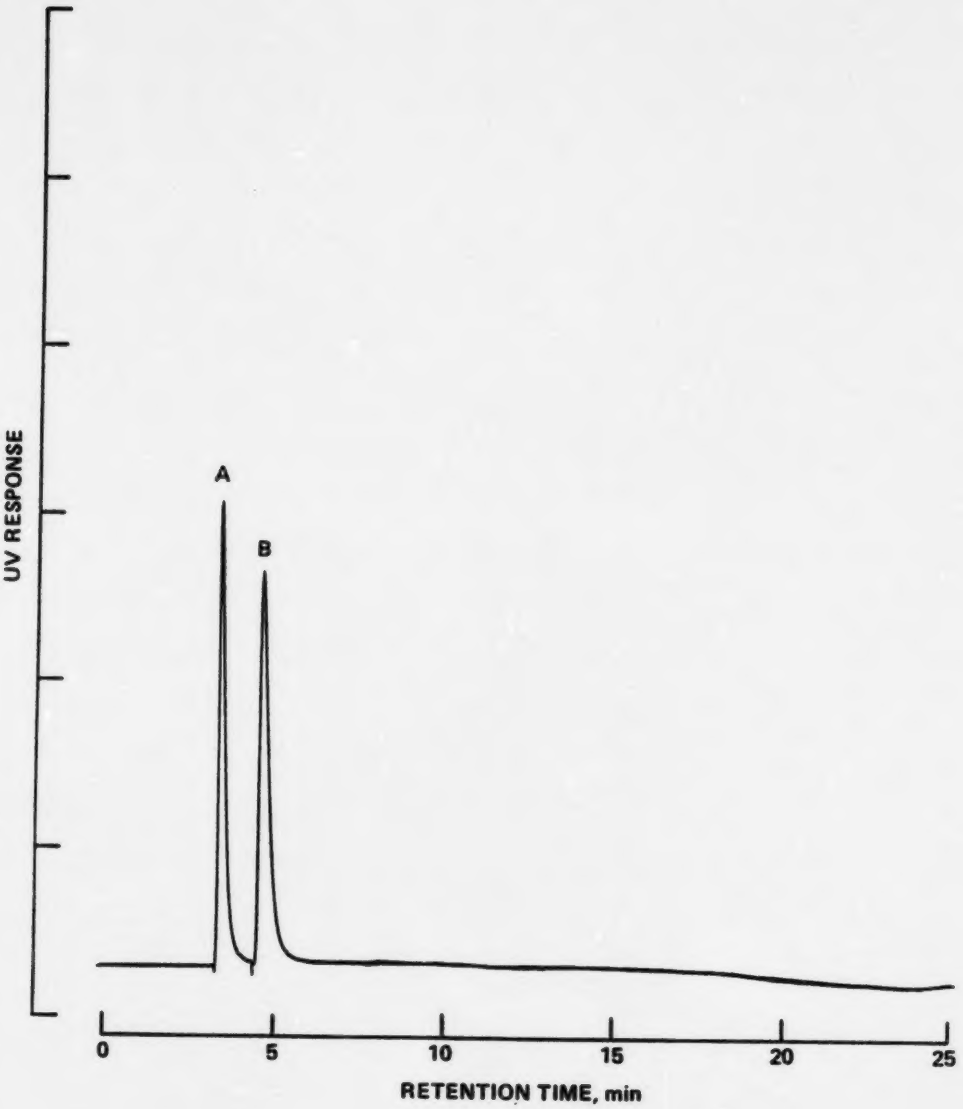

Figure C-89. Chromatogram by HPLC/UV (254 nm) for

(A) thiosemicarbazide(t_R = 3.6 min) and
(B) ethylene thiourea(t_R = 4.8 min).

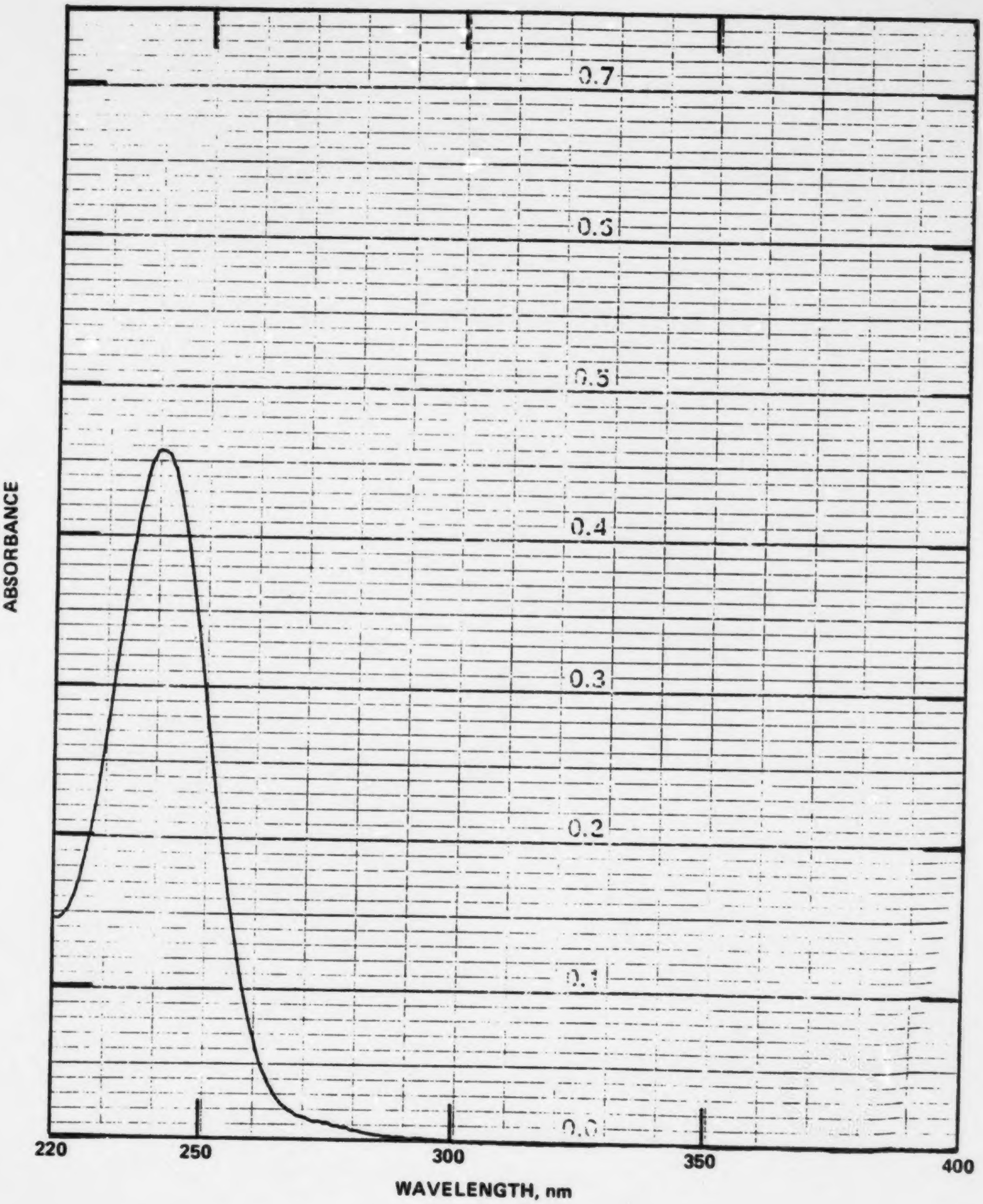

Figure C-90. UV spectrum for thiosemicarbazide.

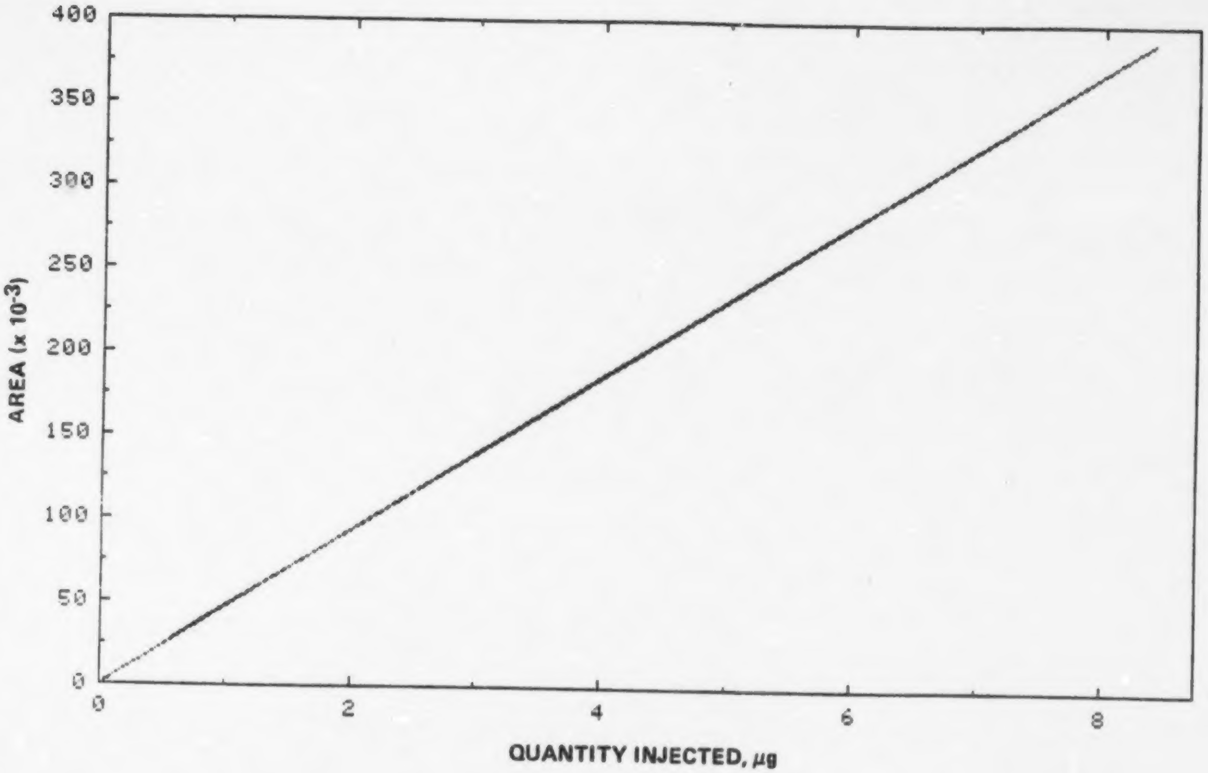

Figure C-91. Calibration curve for the determination of thiosemicarbazide by HPLC/UV.

Range: 0.34 - 8.4 μg
Correlation coefficient: 0.999
Slope: 4.63×10^1
y-Intercept: 6.62×10^{-1}

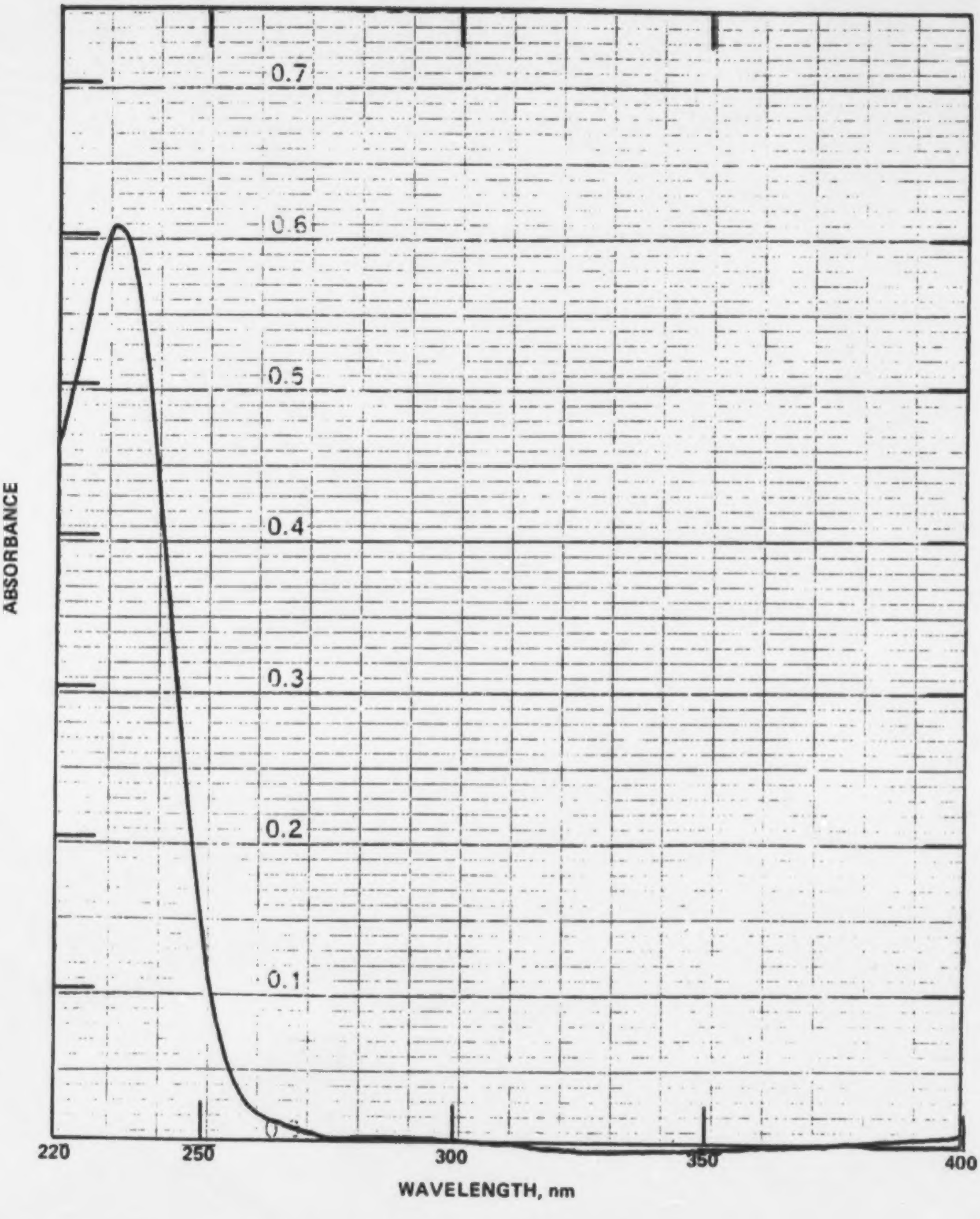

Figure C-92. UV spectrum for ethylene thiourea.

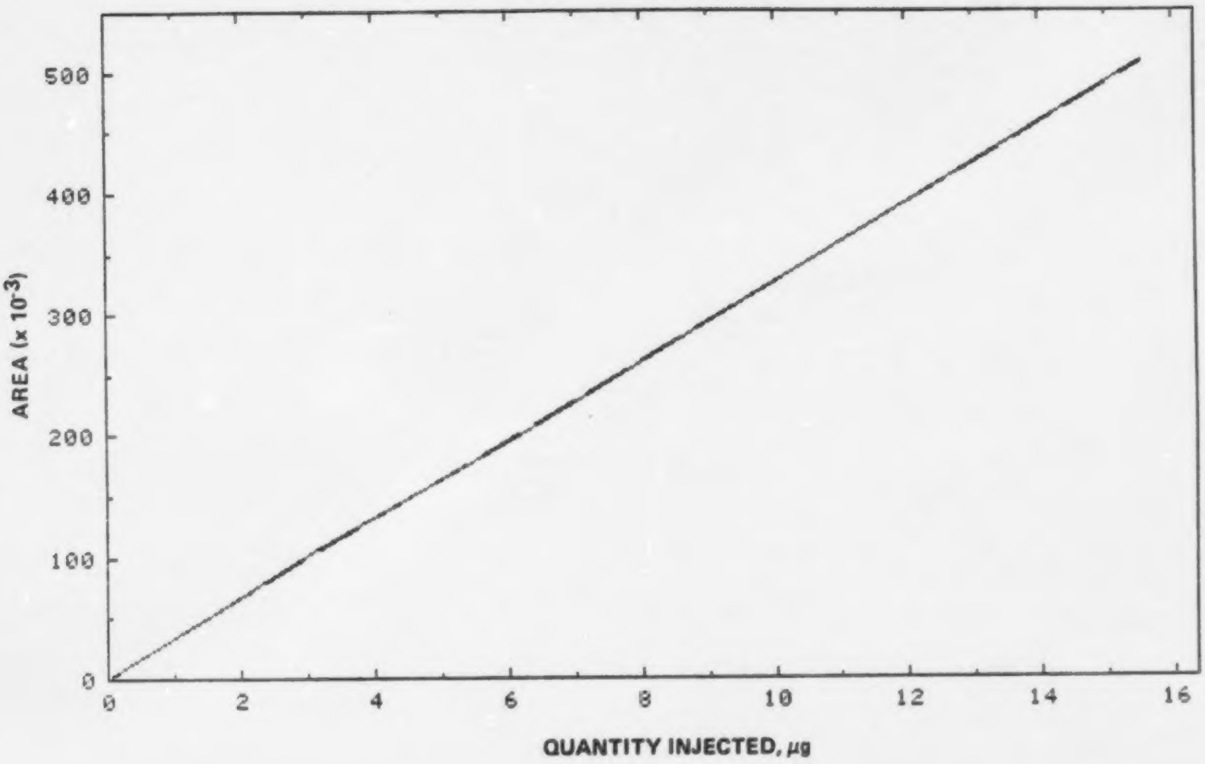

Figure C-93. Calibration curve for the determination of ethylene thiourea by HPLC/UV (254 nm).

Range: 0.16 - 16 µg
Correlation coefficient: 0.999
Slope: 3.26×10^{1}
y-Intercept: 9.32×10^{-1}

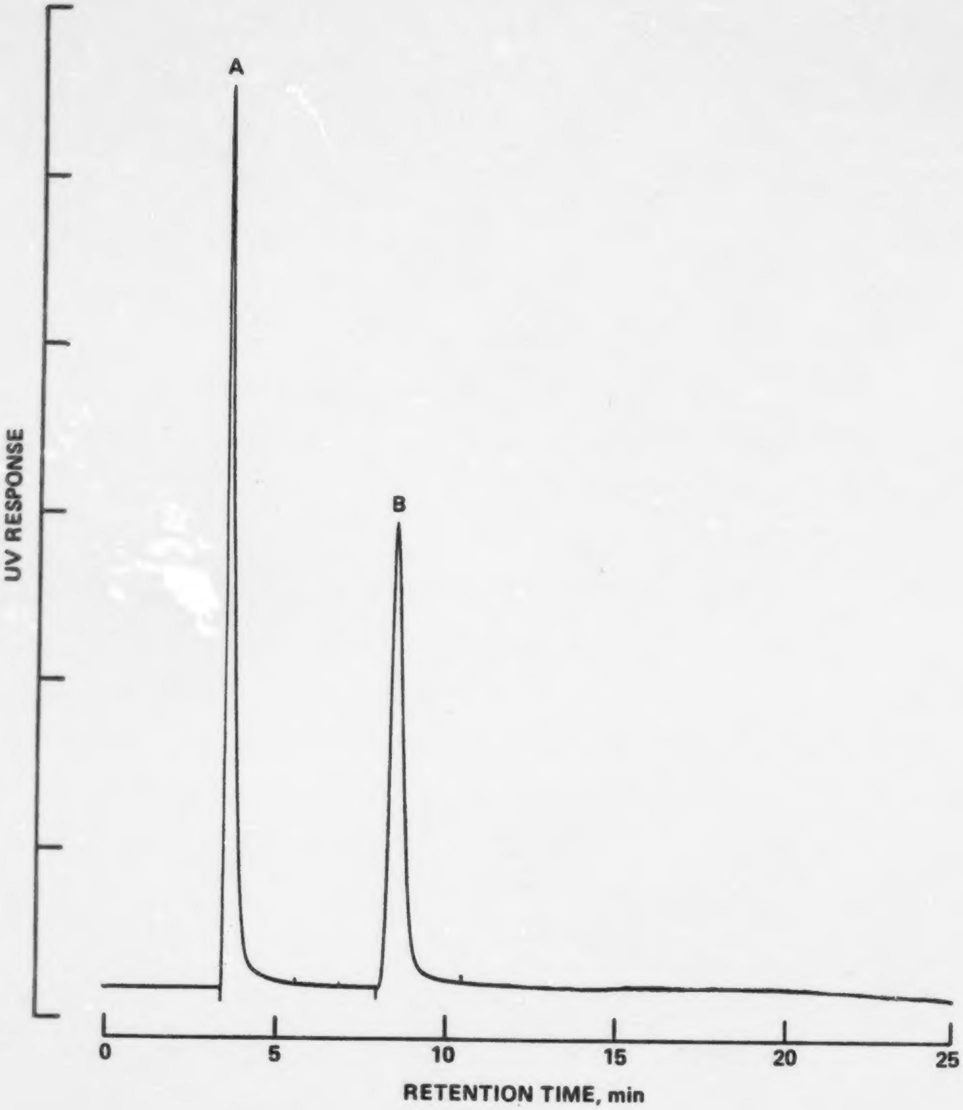

Figure C-94. Chromatogram by HPLC/UV for

(A) azaserine (254 nm) (t_R = 3.6 min) and
(B) resorcinol (273 nm) (t_R = 8.6 min).

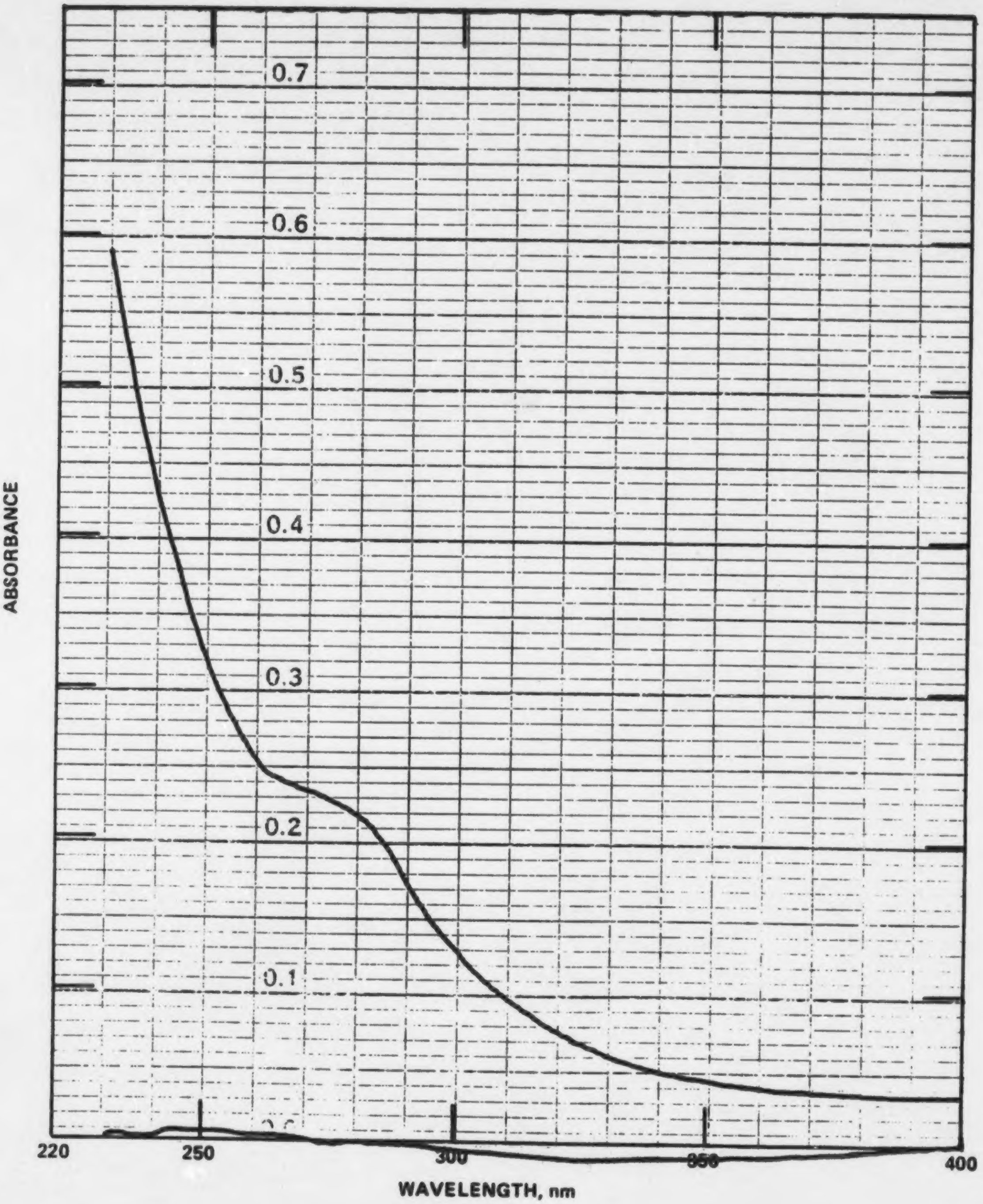

Figure C-95. UV spectrum for azaserine.

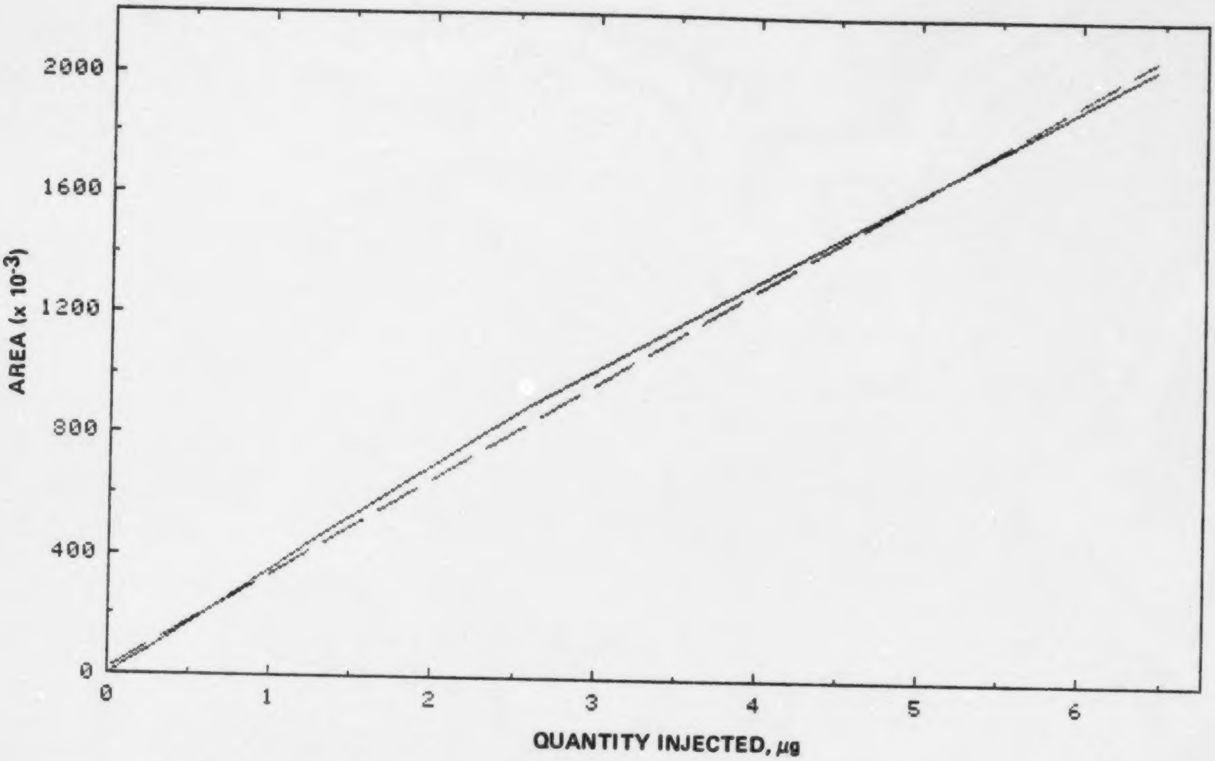

Figure C-96. Calibration curve for the determination of azaserine by HPLC/UV (254 nm).

Range: 0.13 - 6.4 µg
Correlation coefficient: 0.999
Slope: 3.18×10^2
y-Intercept: 1.84×10^1

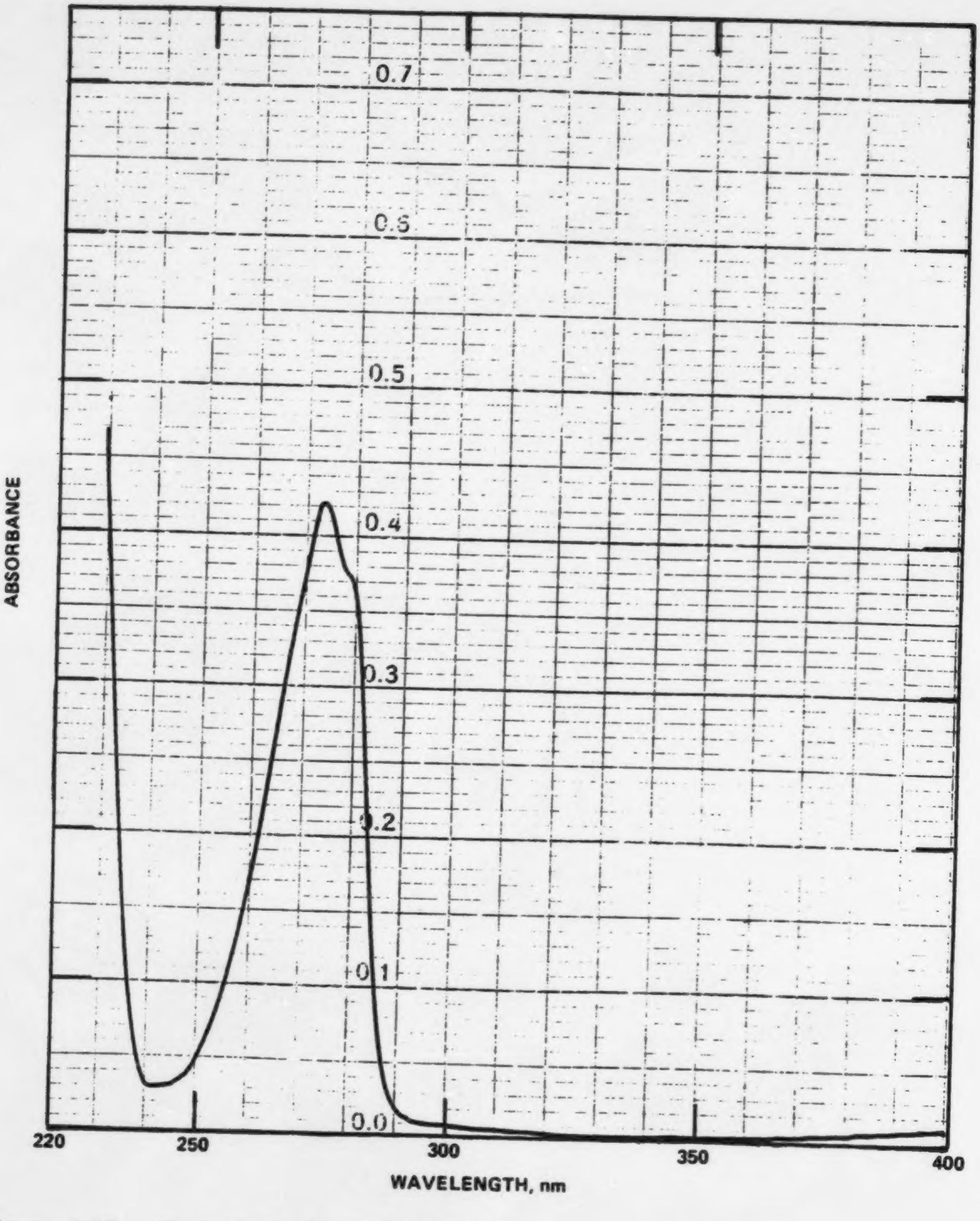

Figure C-97. UV spectrum for resorcinol.

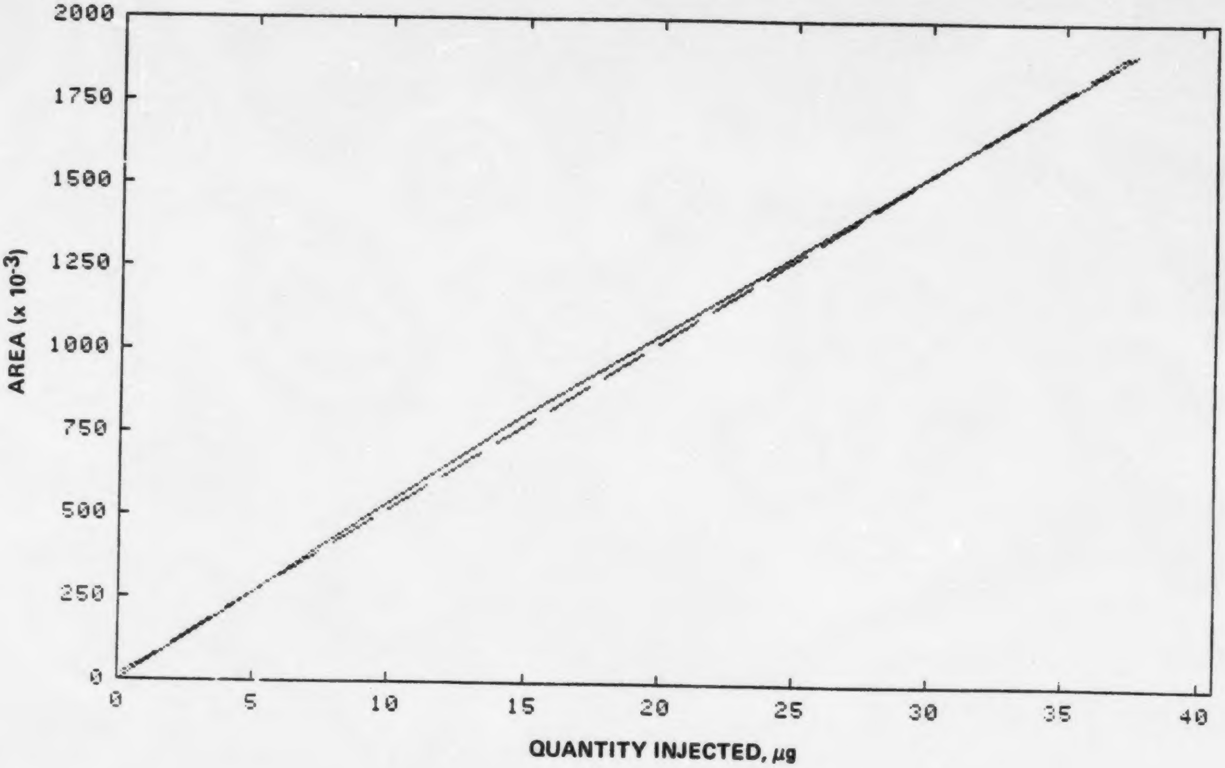

Figure C-98. Calibration curve for the determination of resorcinol by HPLC/UV (273 nm).

Range: 0.38 - 38 μg
Correlation coefficient: 0.999
Slope: 5.08×10^1
y-Intercept: 1.05×10^1

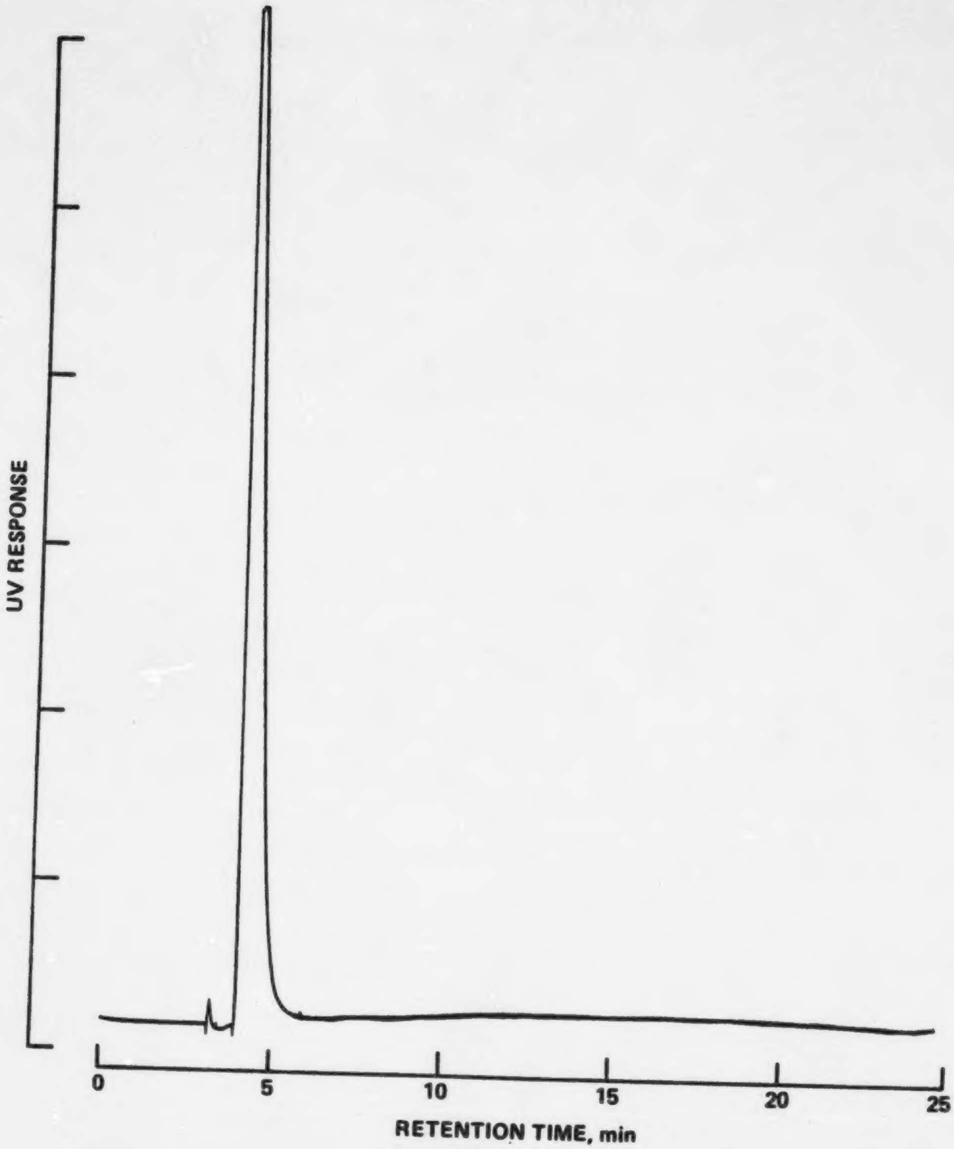

Figure C-99. Chromatogram by HPLC/UV (280 nm) for epinephrine.

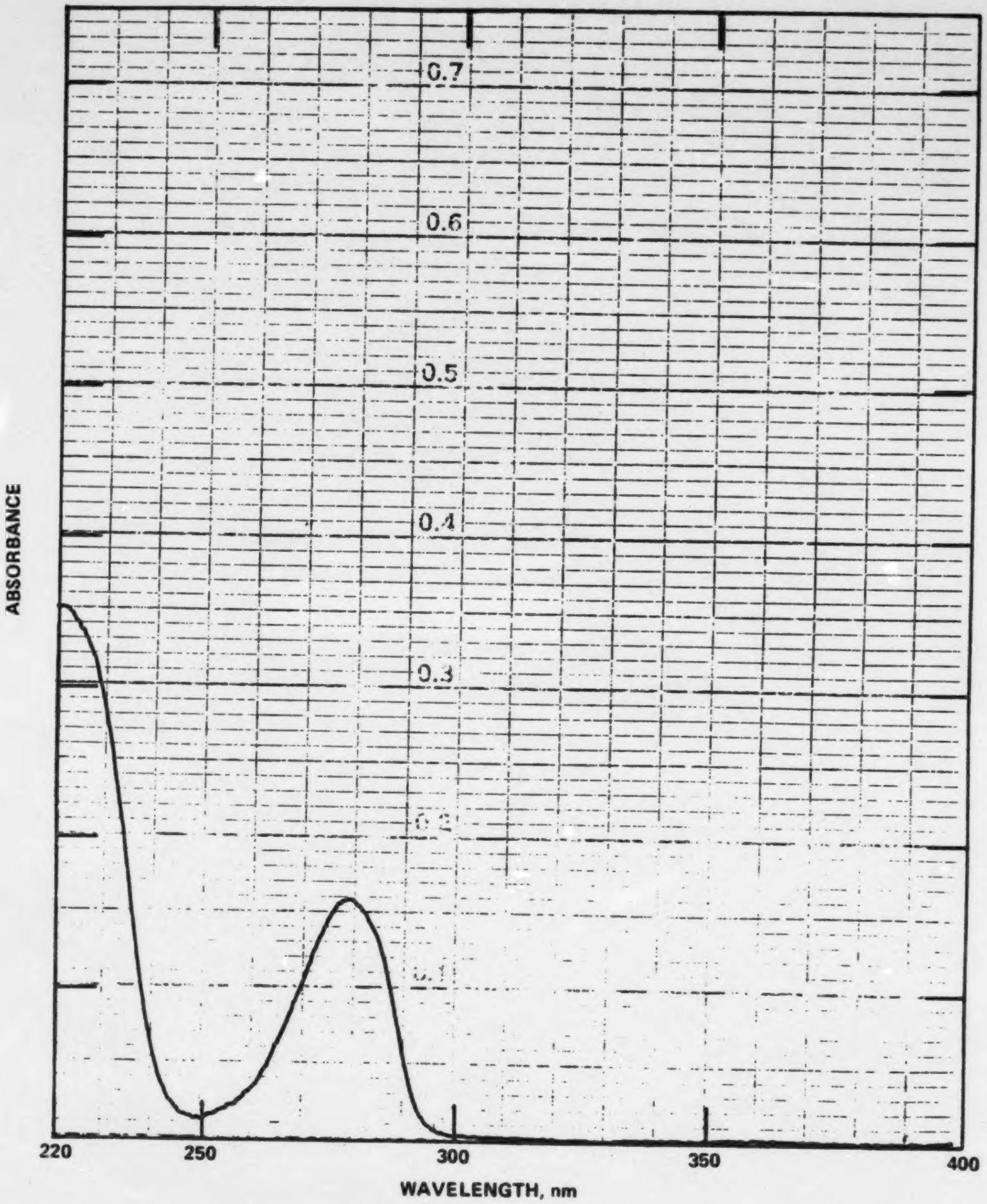

Figure C-100. UV spectrum for epinephrine.

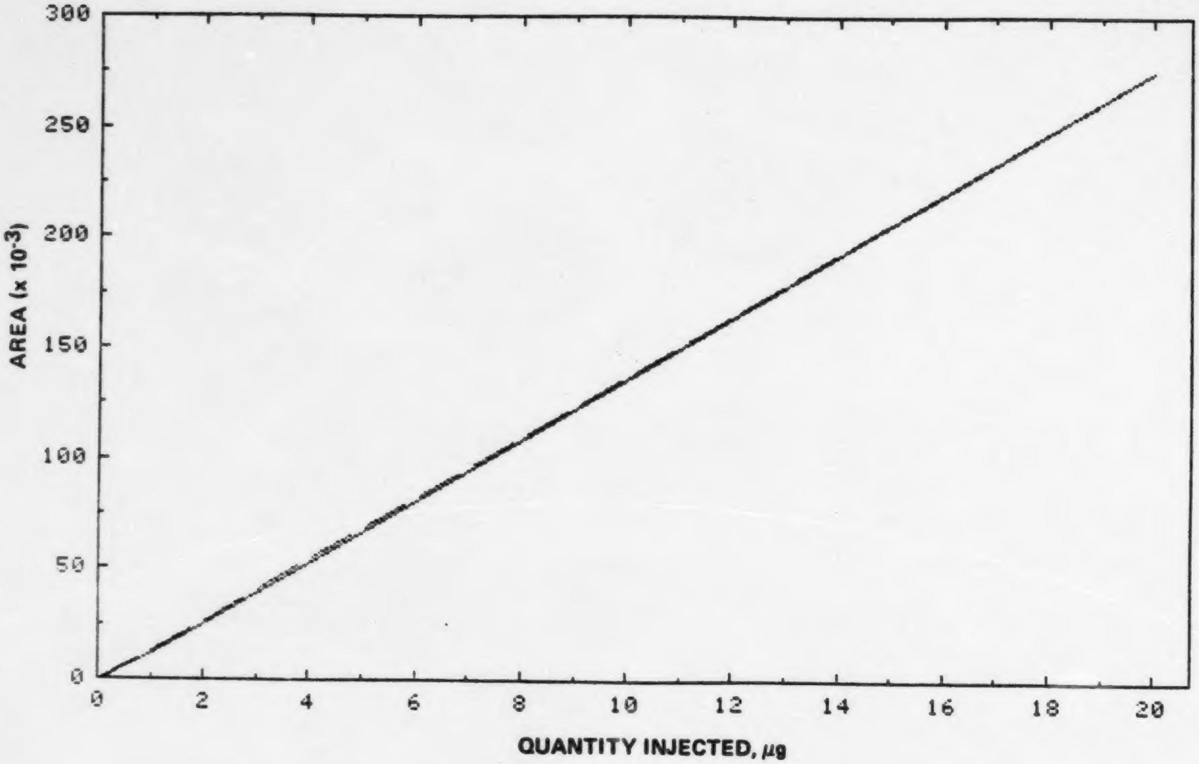

Figure C-101. Calibration curve for the determination of epinephrine by HPLC/UV (280 nm).

Range: 0.40 - 20 μg
Correlation coefficient: 0.999
Slope: 1.38×10^1
y-Intercept: -1.51

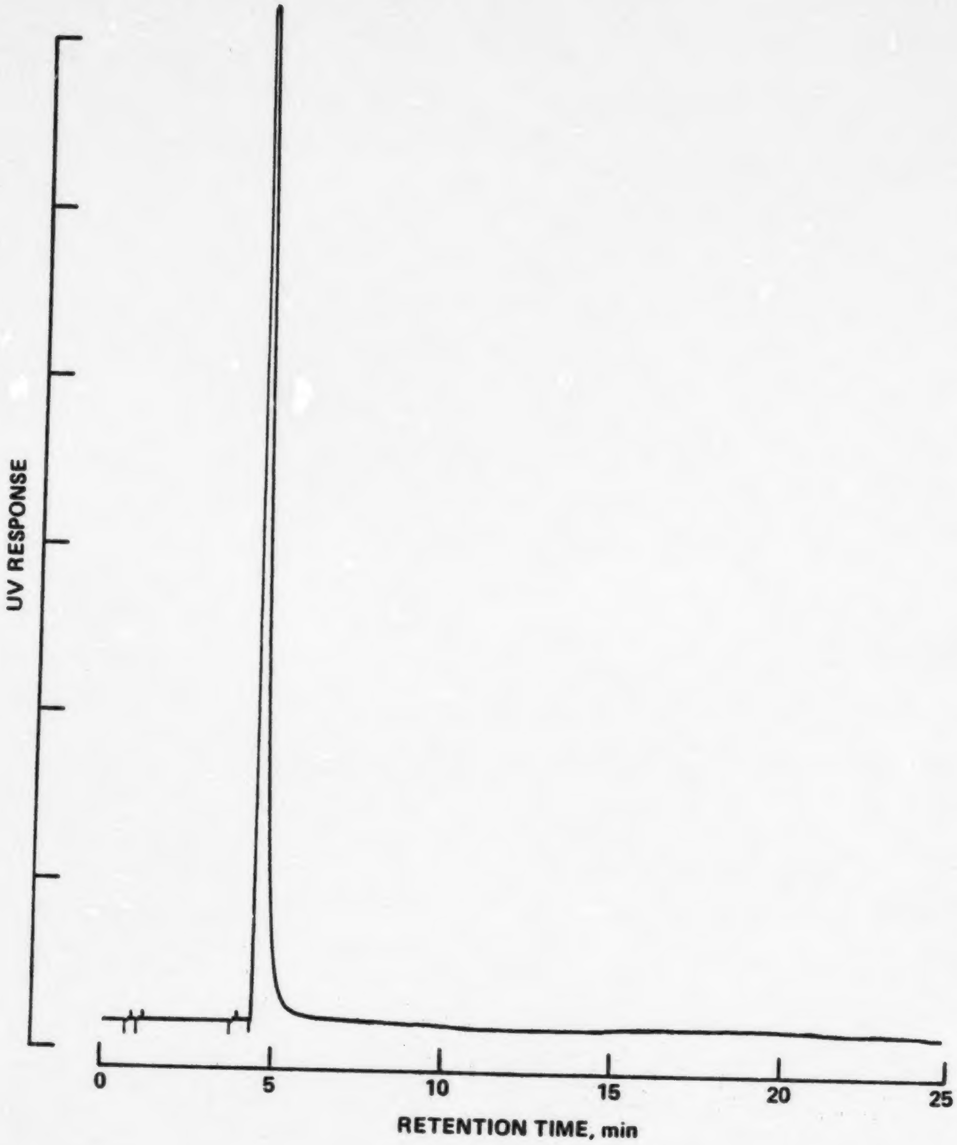

Figure C-102. Chromatogram by HPLC/UV (254 nm) for thioacetamide.

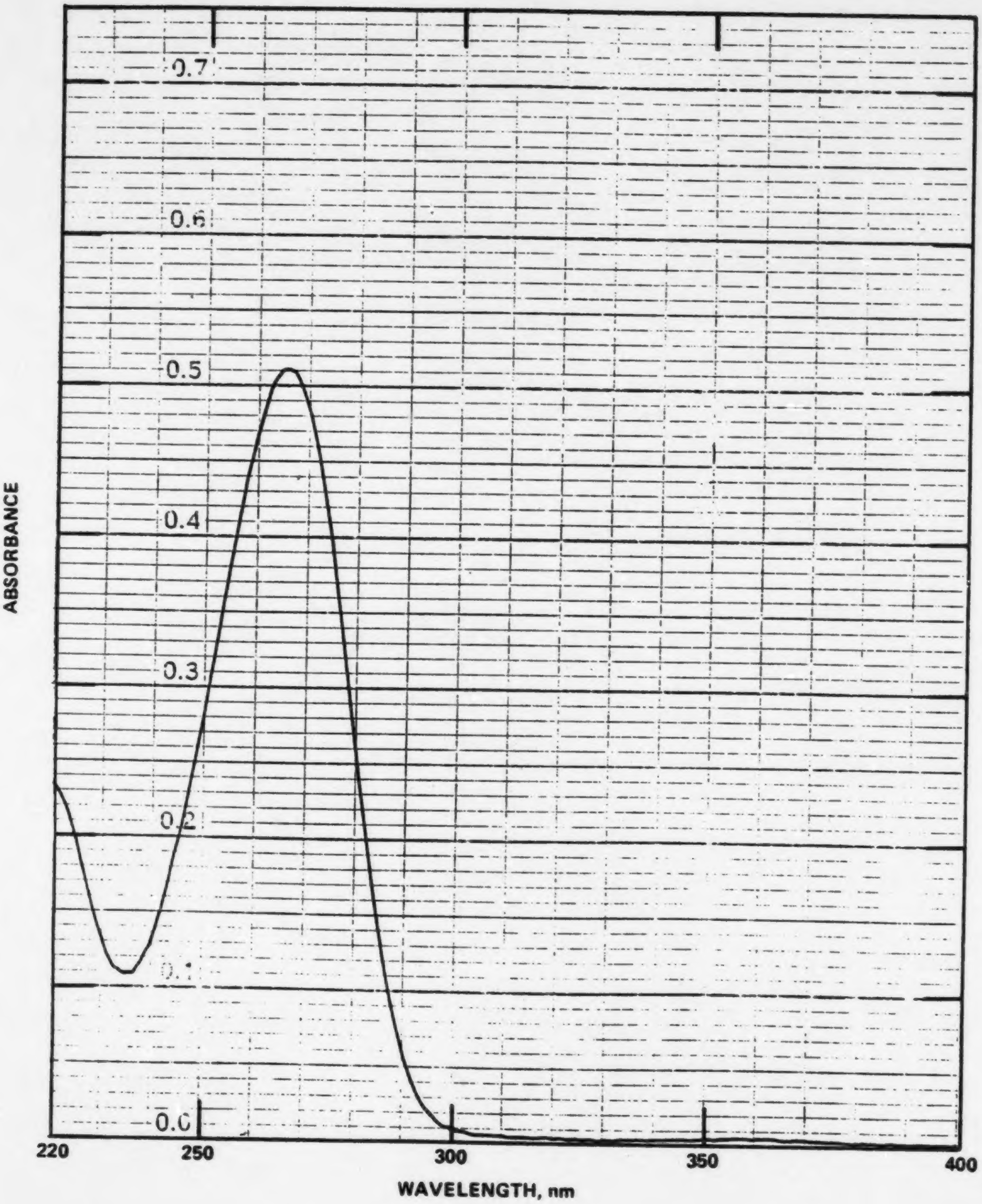

Figure C-103. UV spectrum for thioacetamide.

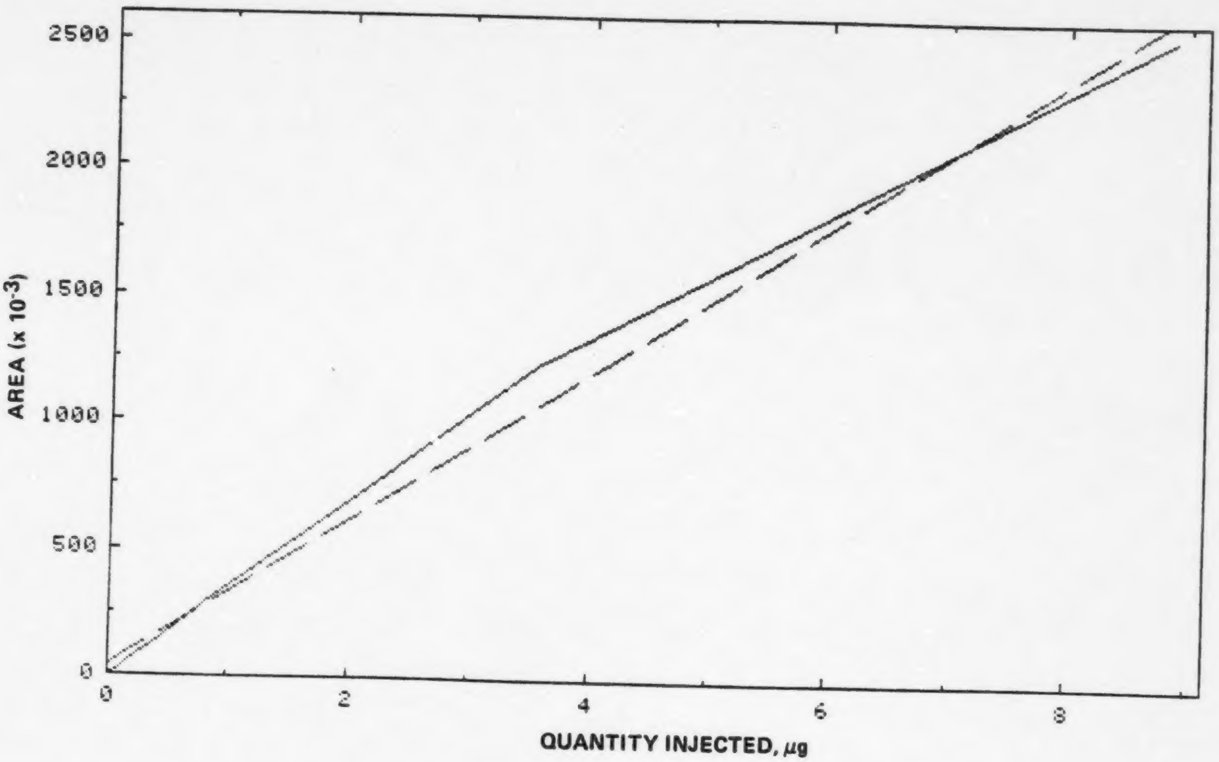

Figure C-104. Calibration curve for the determination of thioacetamide by HPLC/UV (254 nm).

Range: 0.18 - 8.9 µg
Correlation coefficient: 0.996
Slope: 2.90×10^2
y-Intercept: 3.95×10^1

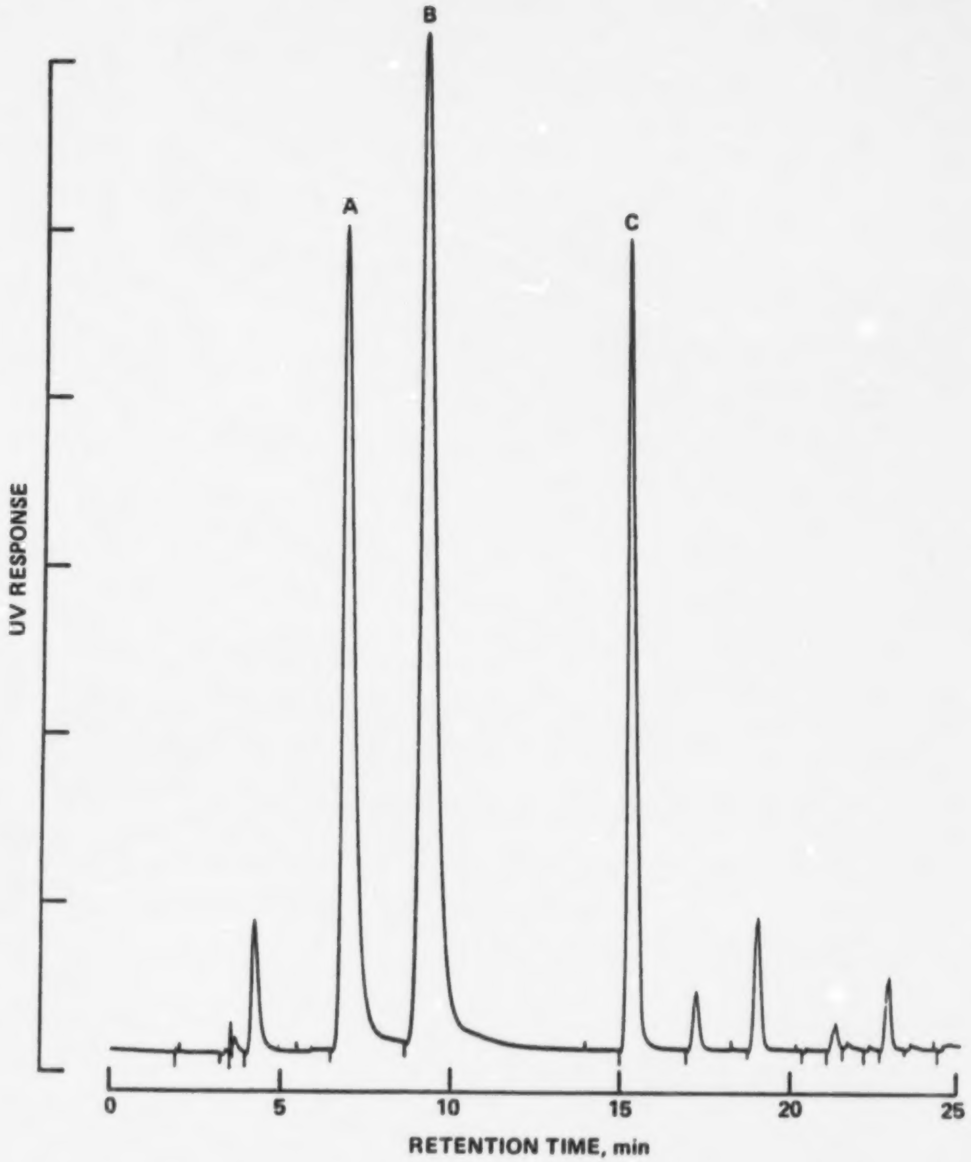

Figure C-105. Chromatogram by HPLC/UV (254 nm) for

(A) phenylthiourea(t_R = 7.2 min),
(B) 1-(2-chlorophenyl)thiourea(t_R = 9.5 min), and
(C) 1-naphthyl-2-thiourea(t_R = 15.5 min).

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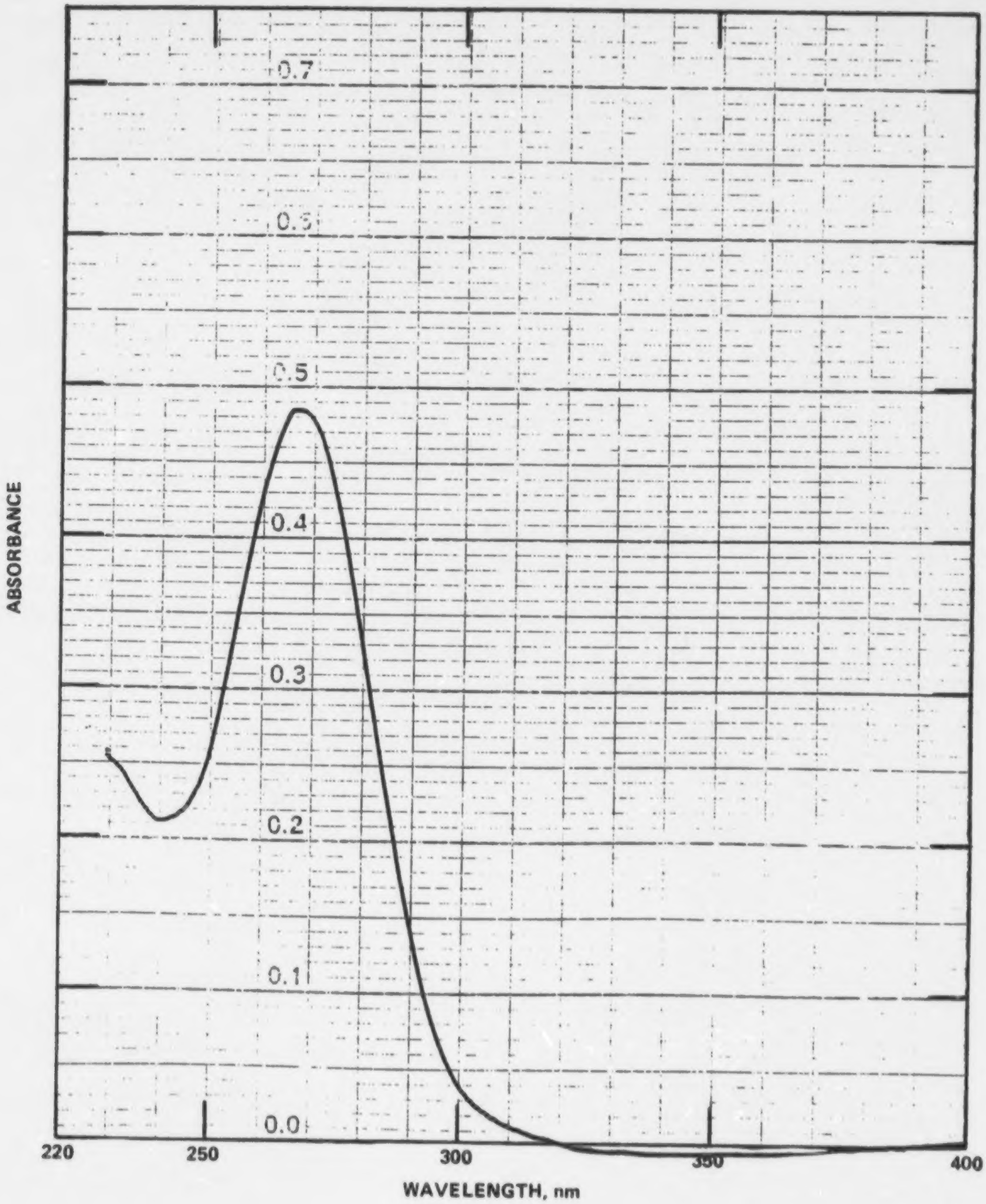

Figure C-106. UV spectrum for phenylthiourea.

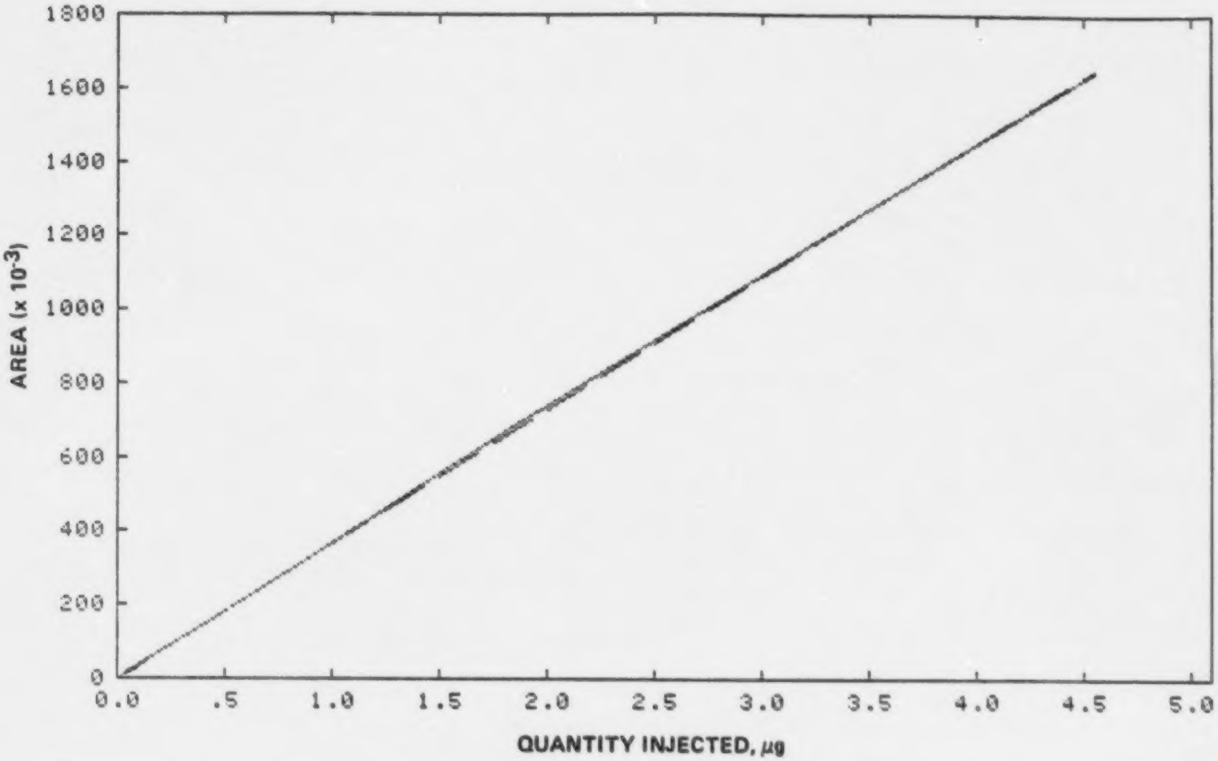

Figure C-107. Calibration curve for the determination of phenylthiourea by HPLC/UV (254 nm).

Range: 0.046 - 4.6 μg
Correlation coefficient: 0.999
Slope: 3.63×10^2
y-Intercept: 8.41×10^{-2}

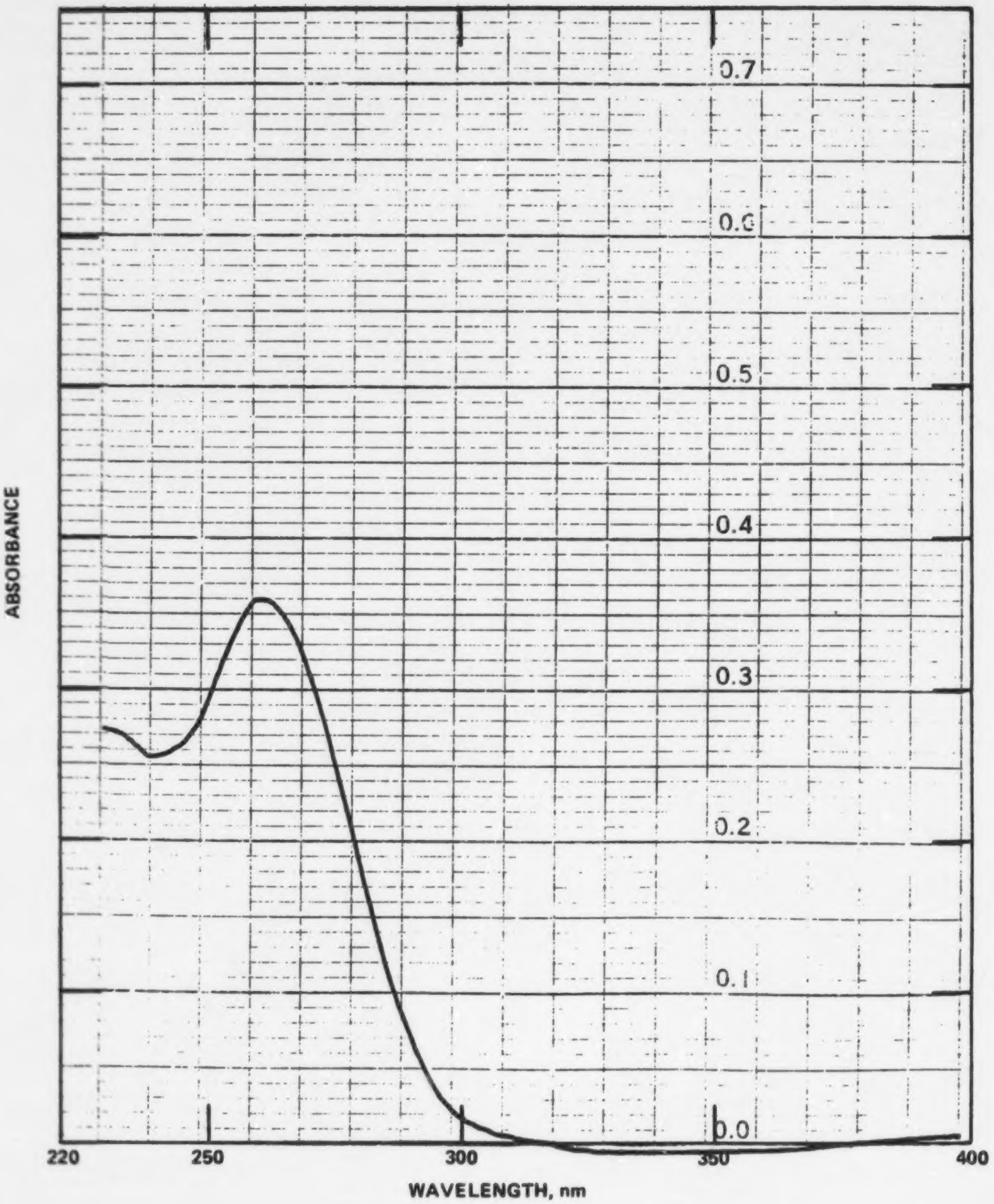

Figure C-108. UV spectrum for 1-(2-chlorophenyl)thiourea.

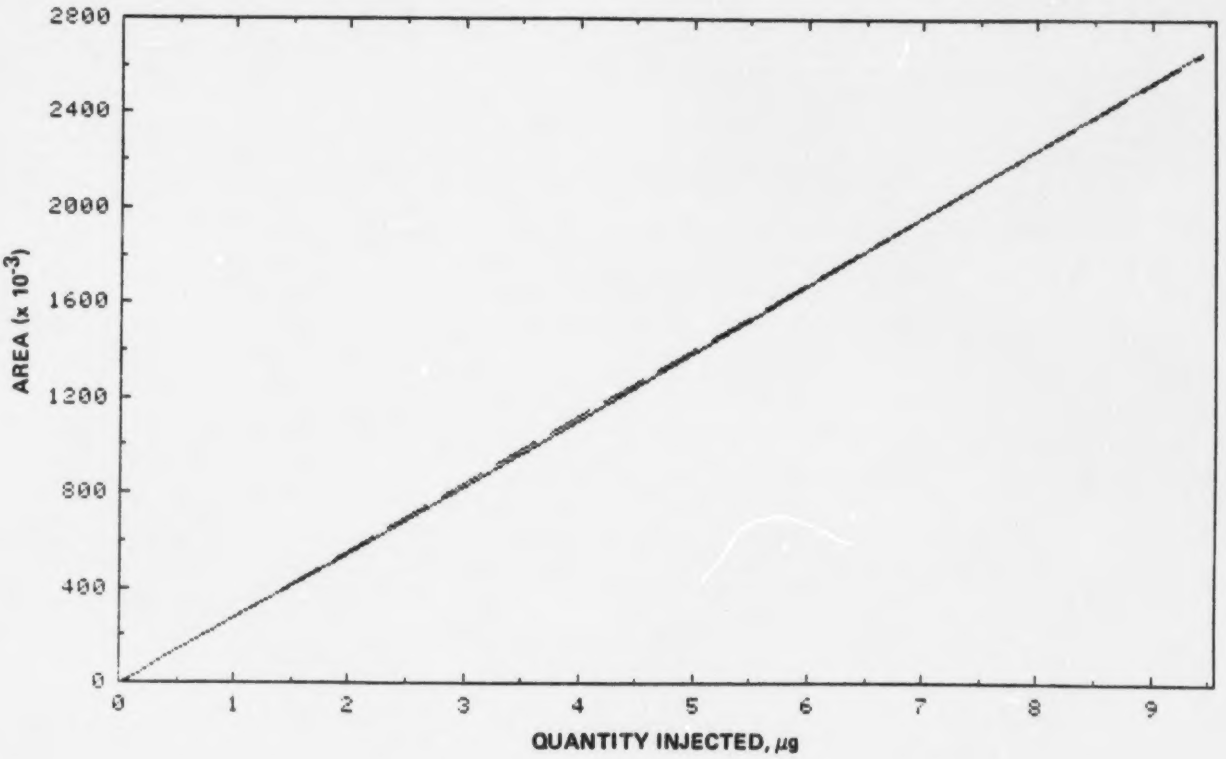

Figure C-109. Calibration curve for the determination of 1-(2-chlorophenyl)thiourea by HPLC/UV (254 nm).

Range: 0.094 - 9.4 µg
Correlation coefficient: 0.999
Slope: 2.82×10^2
y-Intercept: -9.58

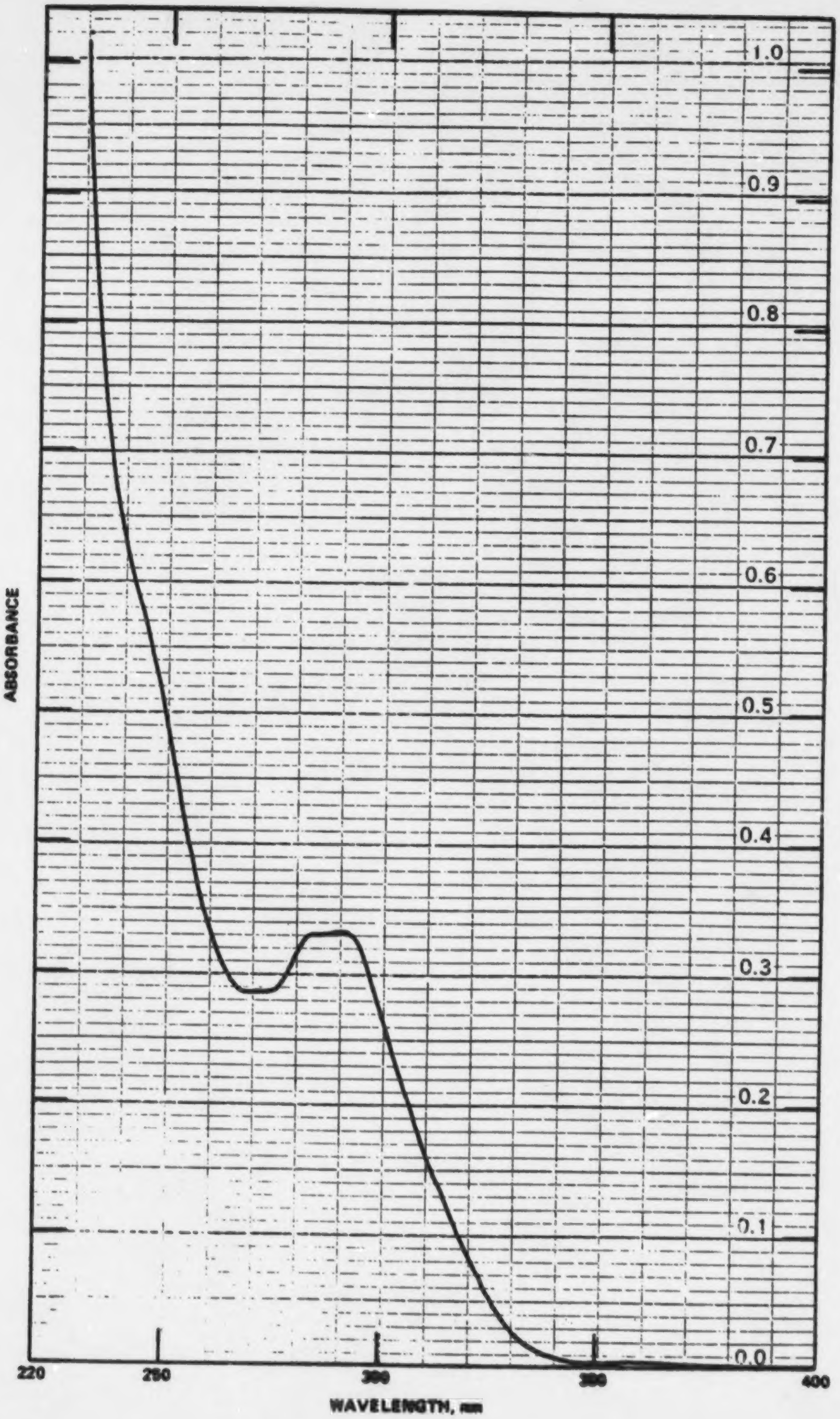

Figure C-110. UV spectrum for 1-naphthyl-2-thiourea.

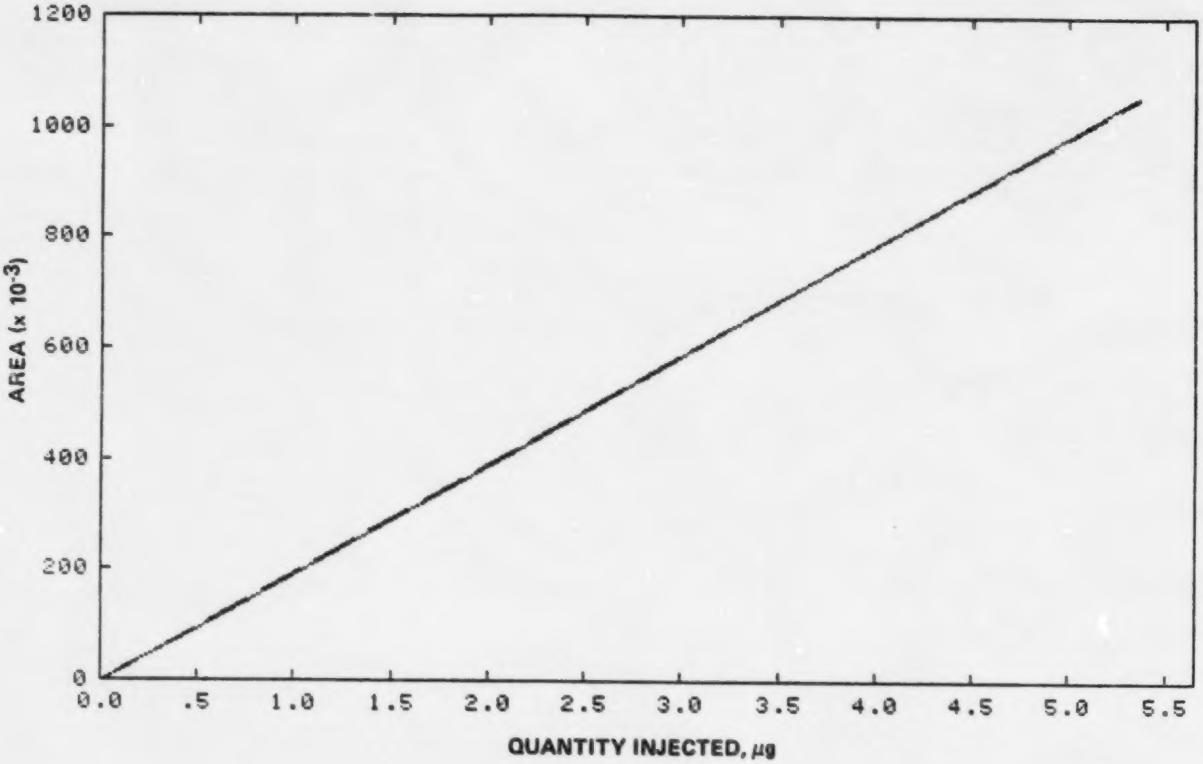

Figure C-111. Calibration curve for the determination of 1-naphthyl-2-thiourea by HPLC/UV (254 nm).

Range: 0.054 - 5.4 µg
Correlation coefficient: 0.999
Slope: 1.97×10^2
y-Intercept: -4.00

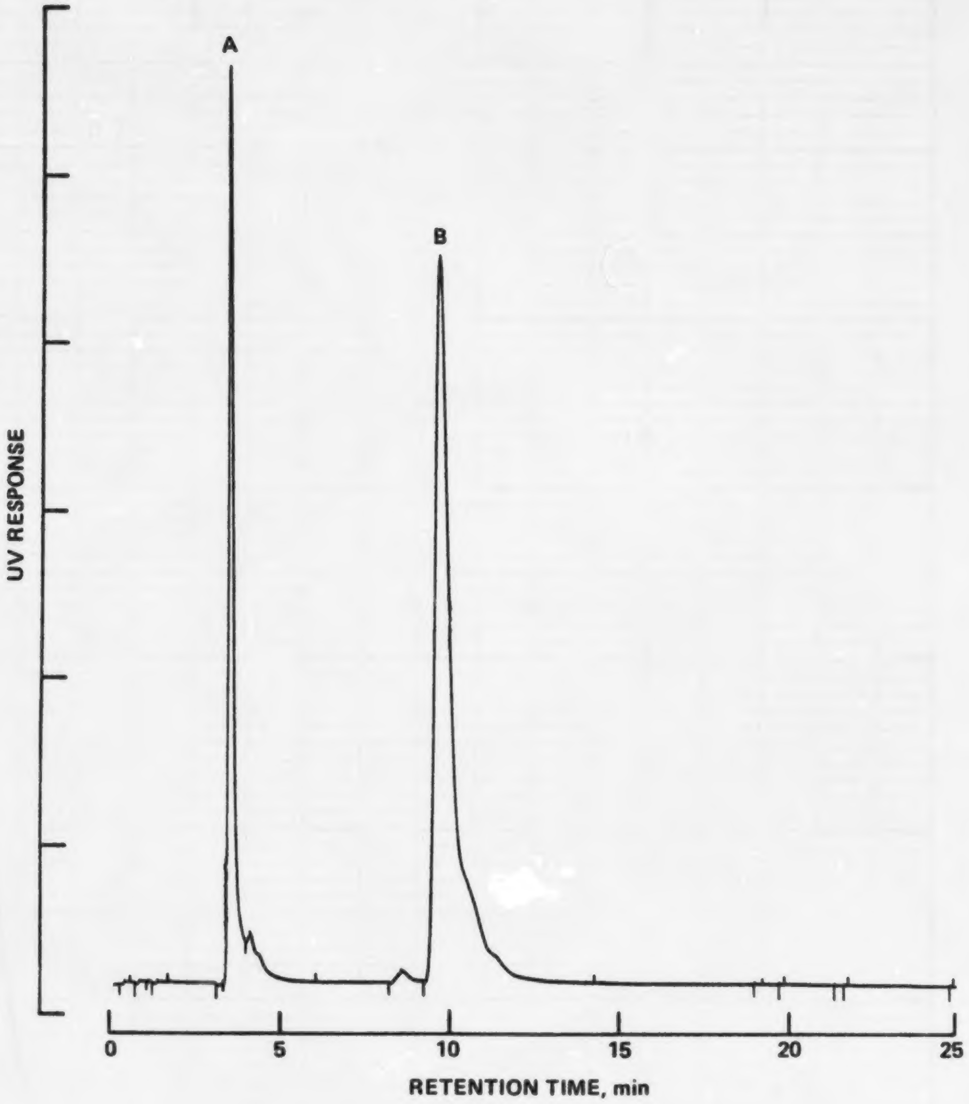

Figure C-112. Chromatogram by HPLC/UV (254 nm) for

(A) saccharin(t_R = 3.4 min) and
(B) brucine(t_R = 9.6 min).

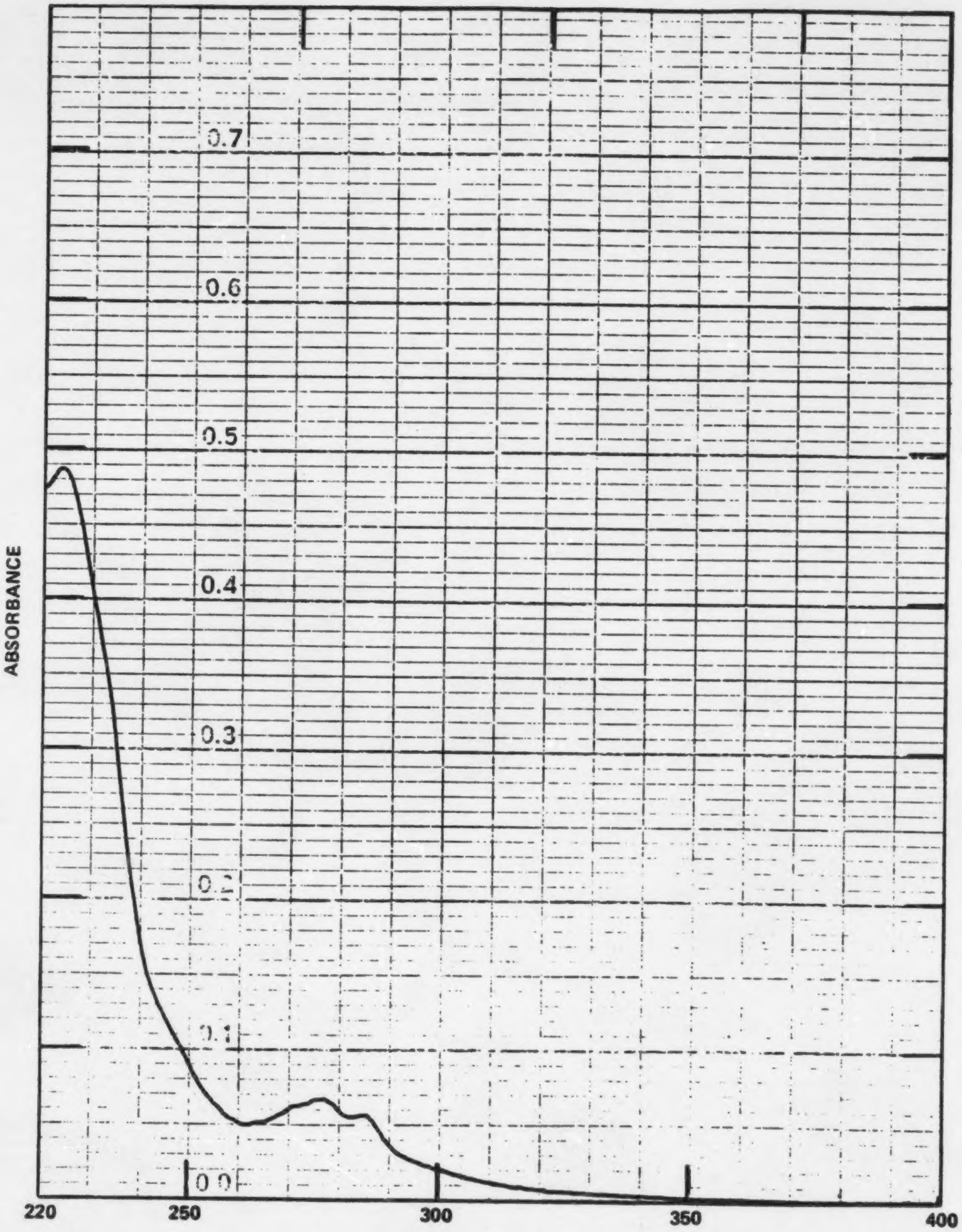

Figure C-113. UV spectrum for saccharin.

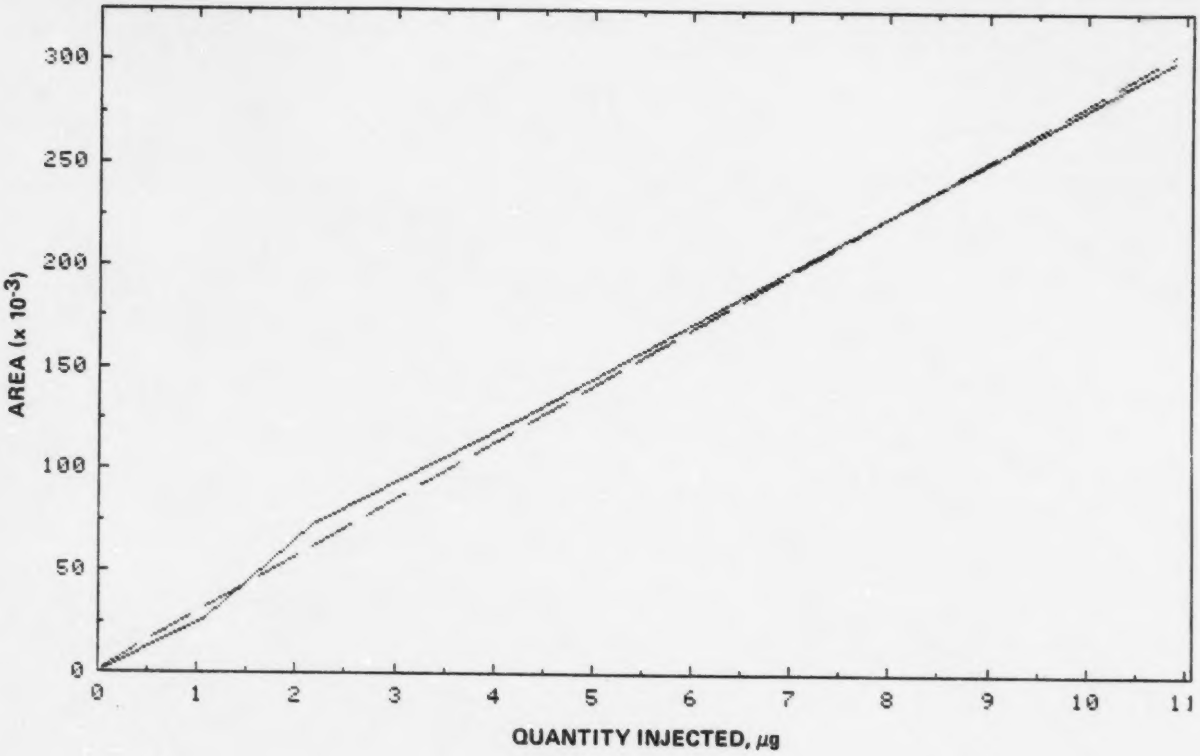

Figure C-114. Calibration curve for the determination of saccharin by HPLC/UV (254 nm).

Range: 0.011 - 11 μg
Correlation coefficient: 0.999
Slope: 2.78×10^1
y-Intercept: 1.33

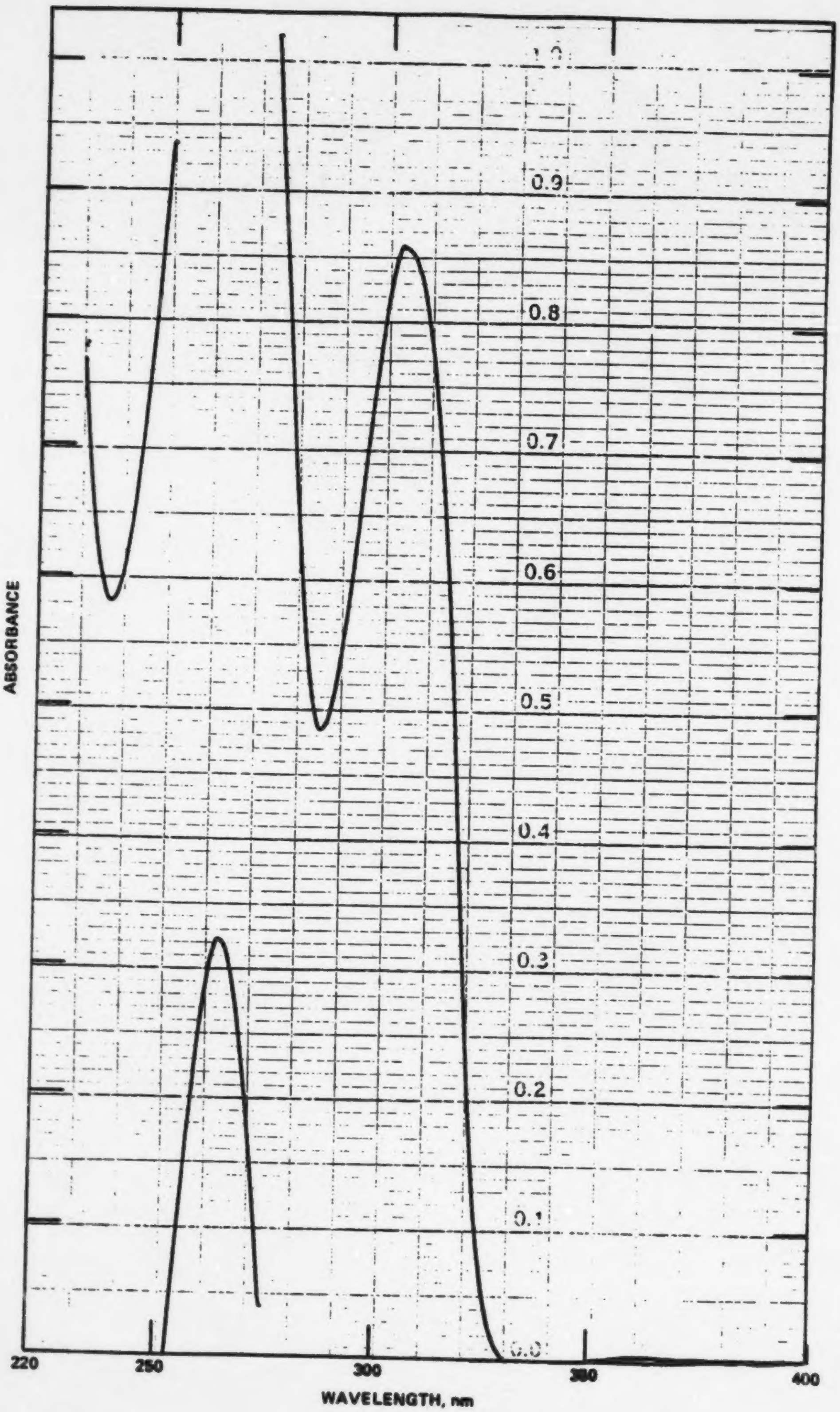

Figure C-115. UV spectrum for brucine.

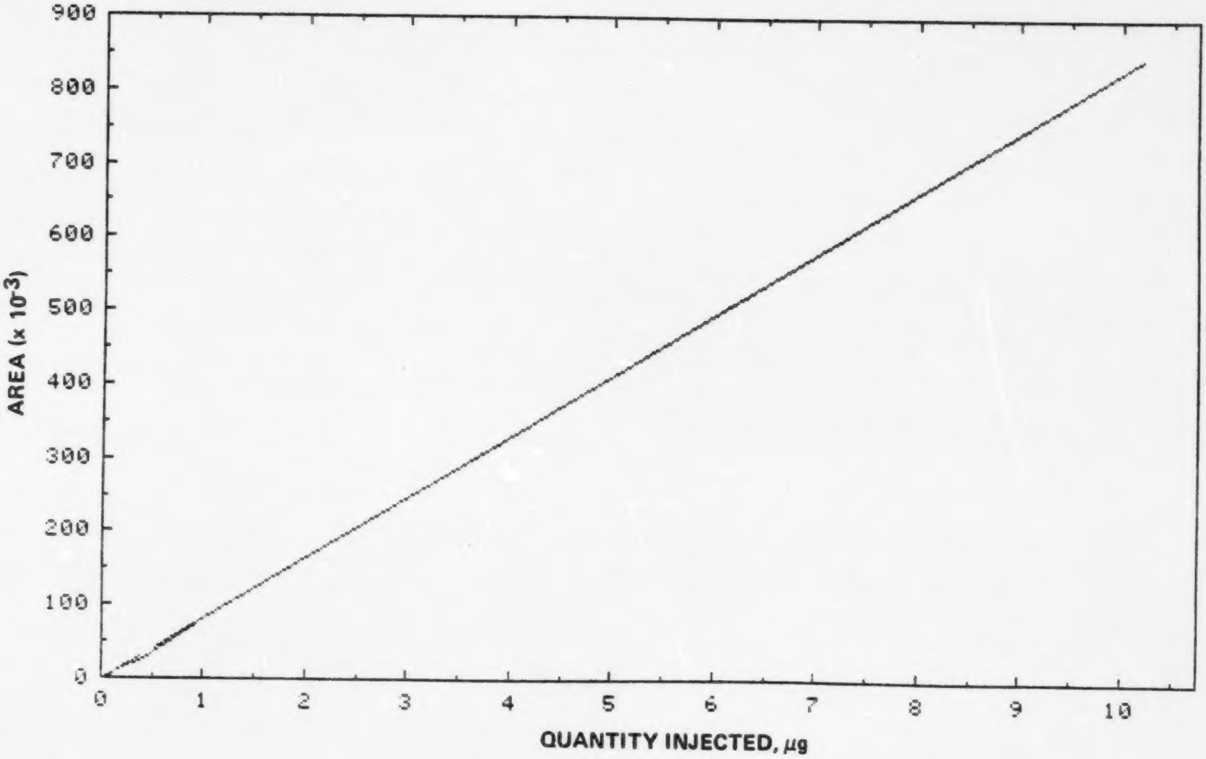

Figure C-116. Calibration curve for the determination of brucine by HPLC/UV (254 nm).

Range: 0.010 - 10 μg
Correlation coefficient: 0.999
Slope: 8.34 x 10^1
y-Intercept: -2.14

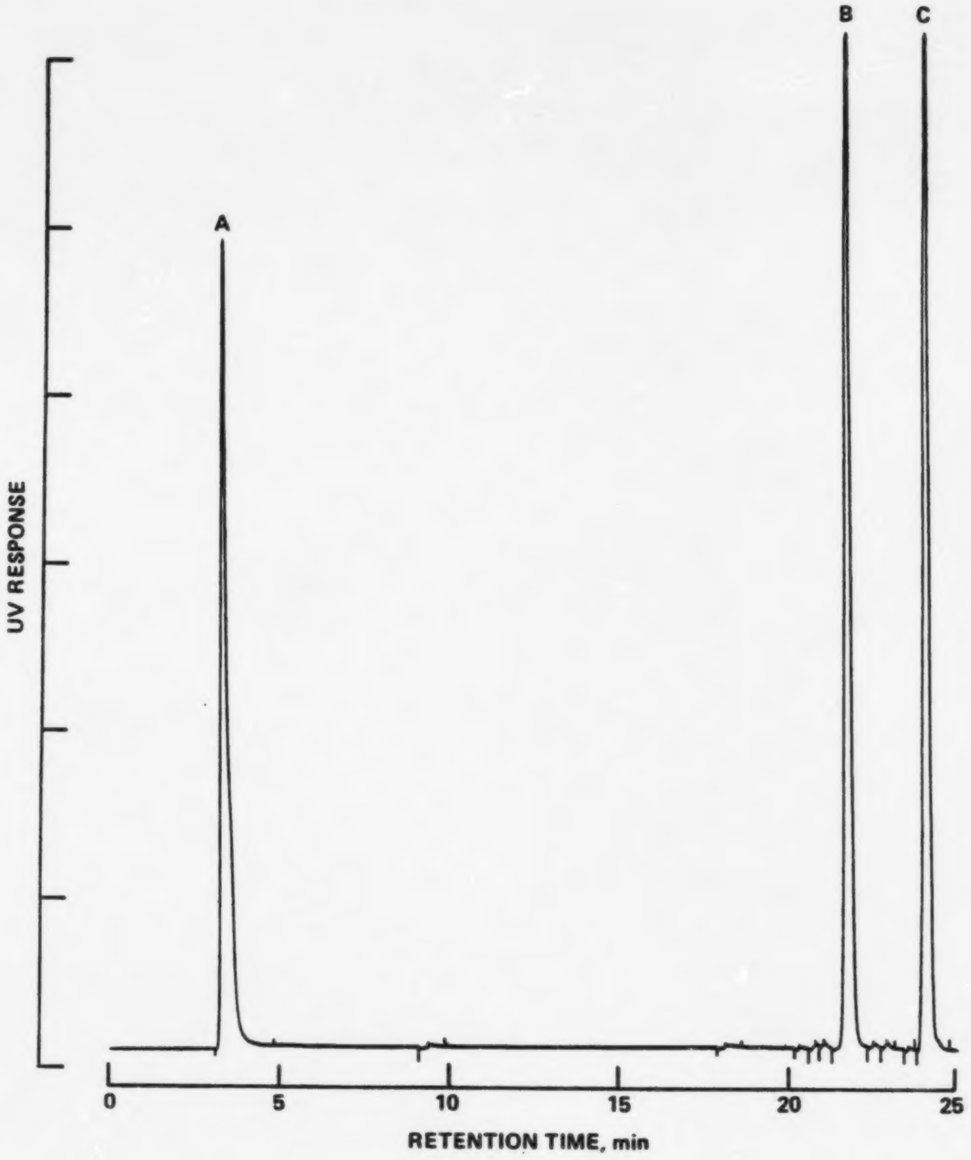

Figure C-117. Chromatogram by HPLC/UV (254 nm) for

(A) streptozotocin(t_R = 3.4 min),
(B) daunomycin(t_R = 21.9 min), and
(C) 4,4'-methylenebis(2-chloroaniline)(t_R = 24.2 min).

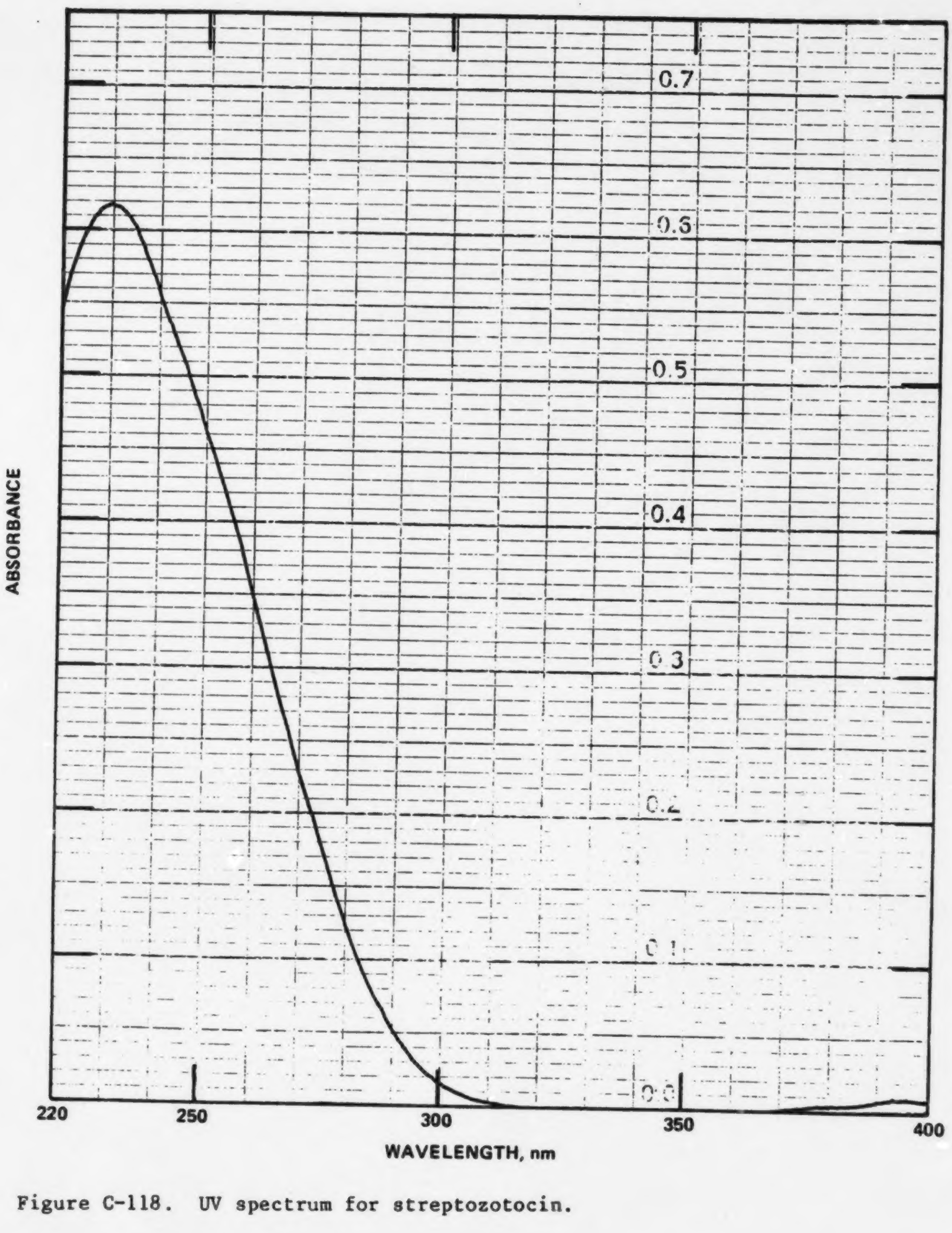

Figure C-118. UV spectrum for streptozotocin.

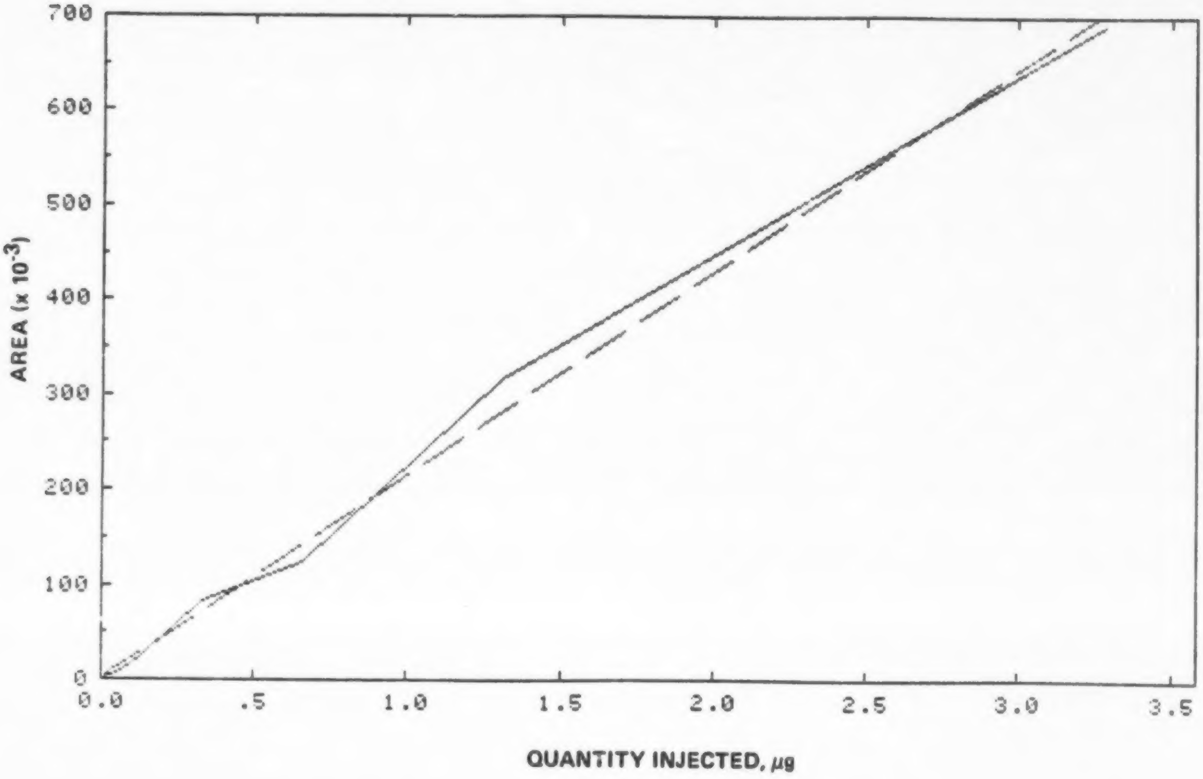

Figure C-119. Calibration curve for the determination of streptozotocin by HPLC/UV (254 nm).

Range: 0.13 - 3.3 μg
Correlation coefficient: 0.998
Slope: 2.14×10^2
y-Intercept: 1.83

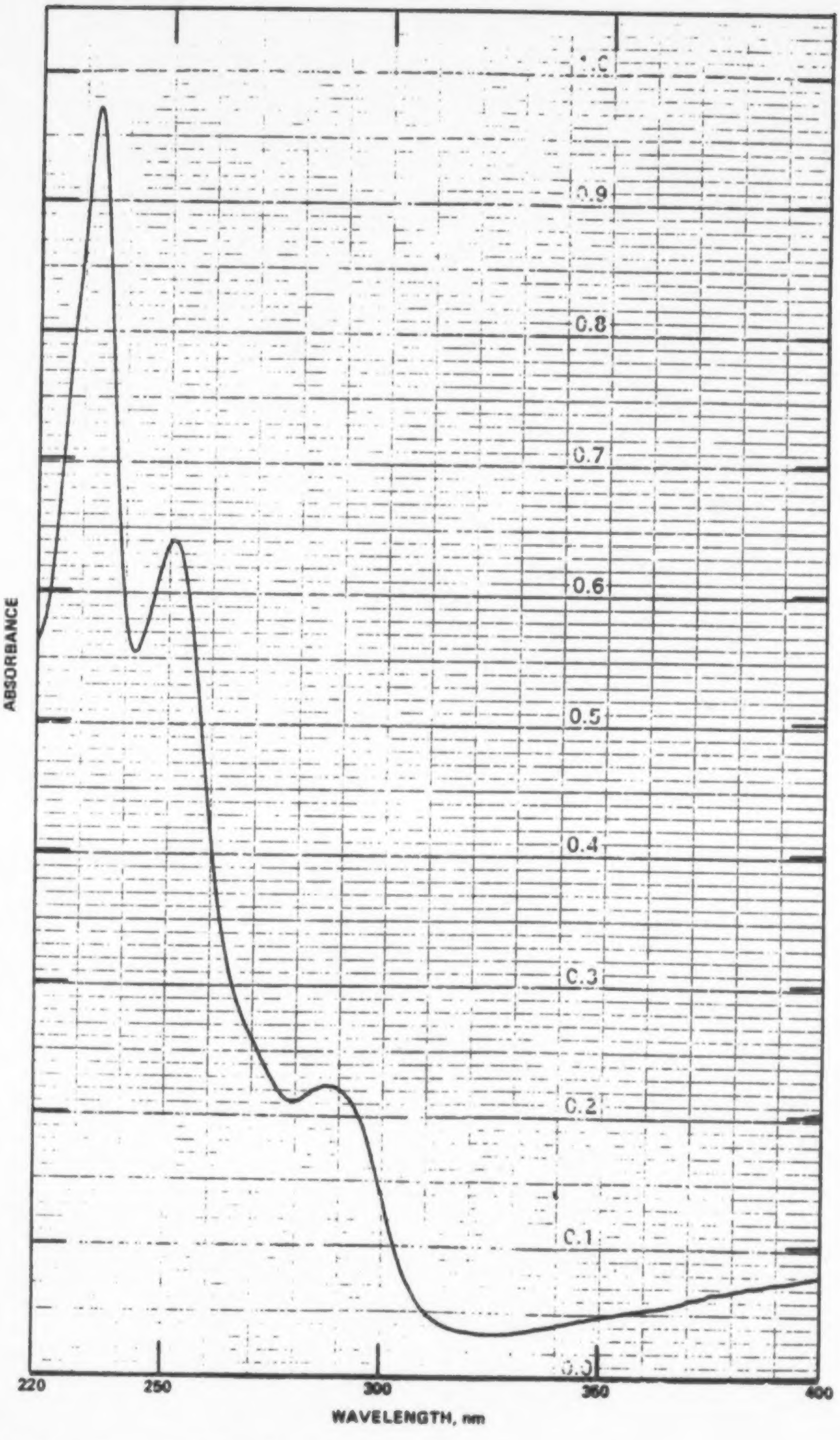

Figure C-120. UV spectrum for daunomycin.

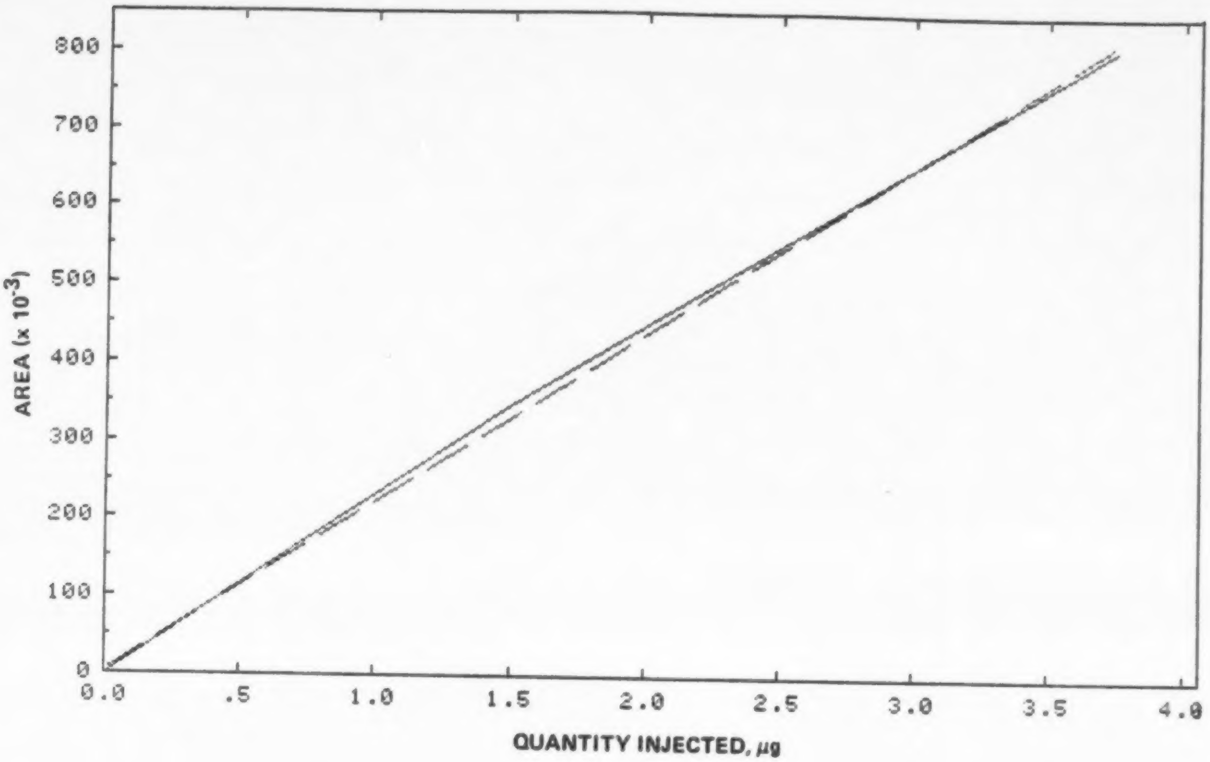

Figure C-121. Calibration curve for the determination of daunomycin by HPLC/UV (254 nm).

Range: 0.075 - 3.8 µg
Correlation coefficient: 0.999
Slope: 2.16×10^2
y-Intercept: 4.39

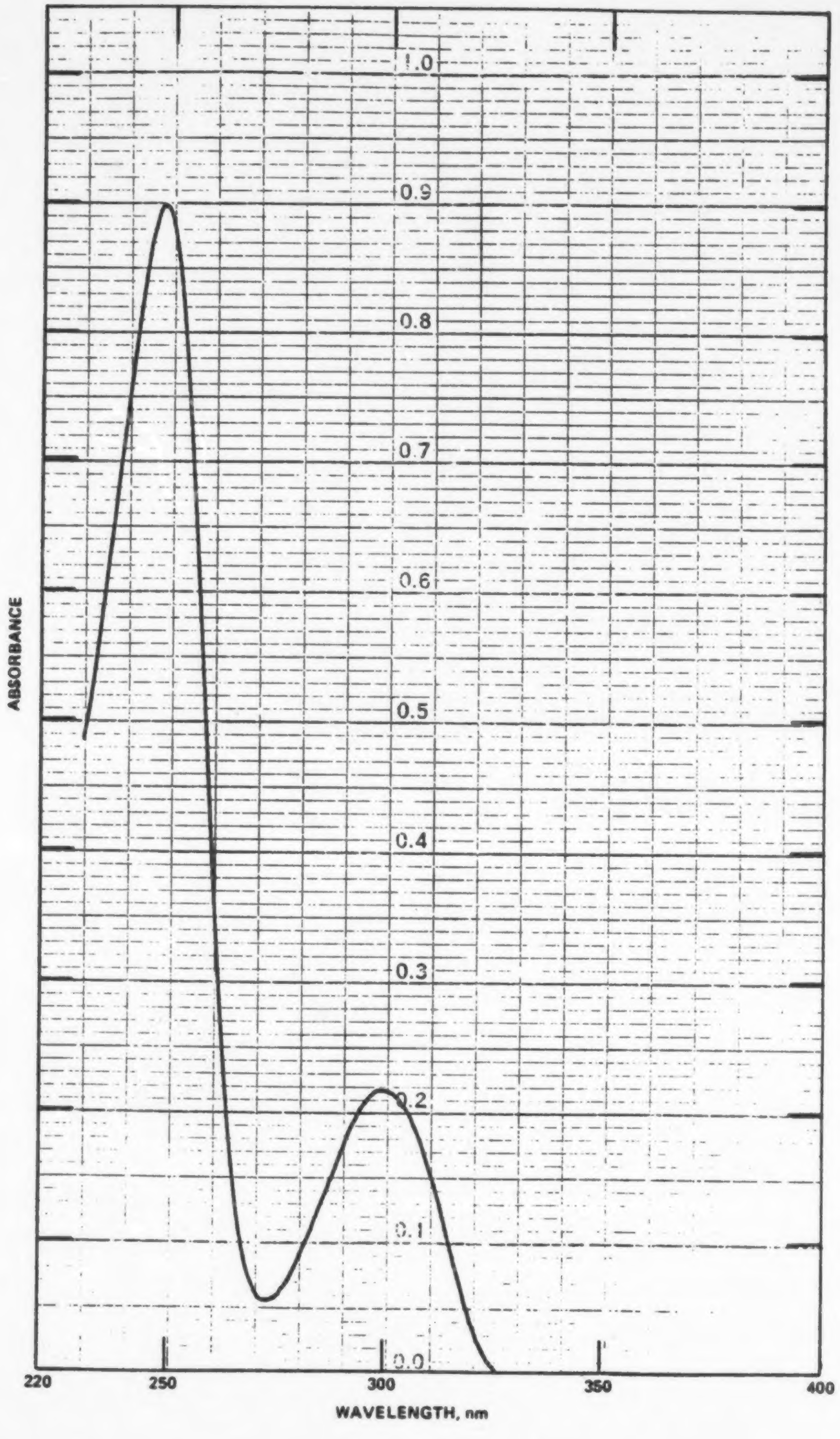

Figure C-122. UV spectrum for 4,4'-methylenebis(2-chloroaniline).

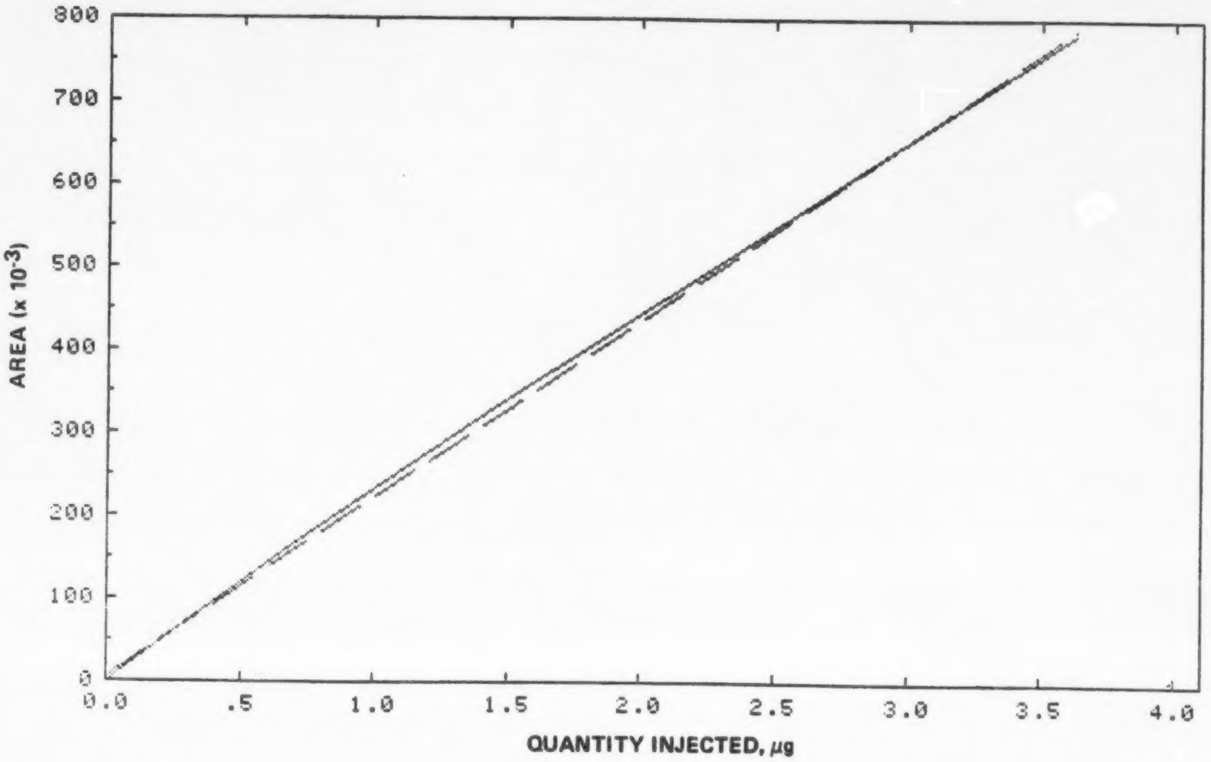

Figure C-123. Calibration curve for the determination of 4,4'-methylenebis(2-chloroaniline) by HPLC/UV (254 nm).

Range: 0.072 - 3.6 µg
Correlation coefficient: 0.999
Slope: 2.16×10^2
y-Intercept: 6.04×10

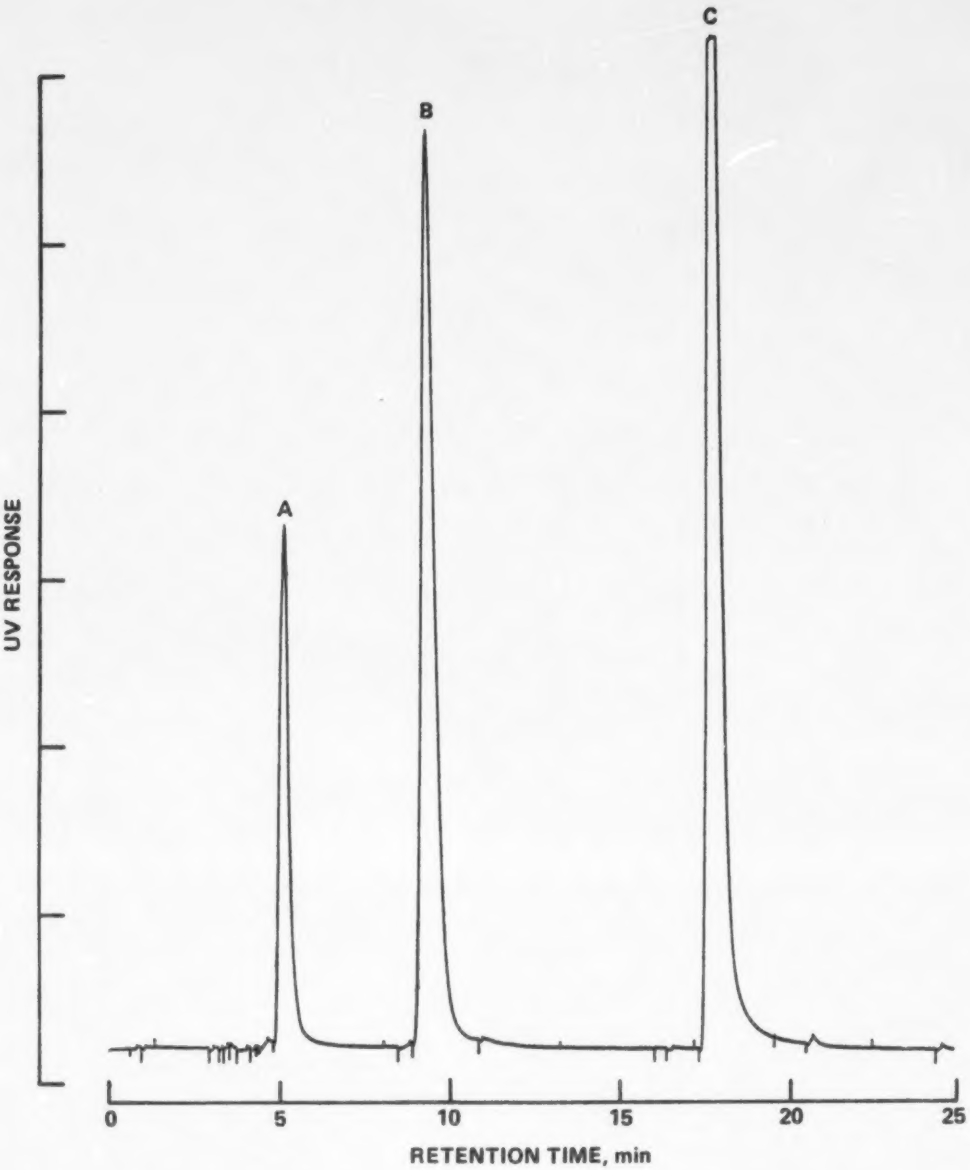

Figure C-124. Chromatogram by HPLC/UV (254 nm) for

(A) nicotine(t_R = 5.1 min),
(B) strychnine(t_R = 9.5 min), and
(C) methapyrilene(t_R = 18.2 min).

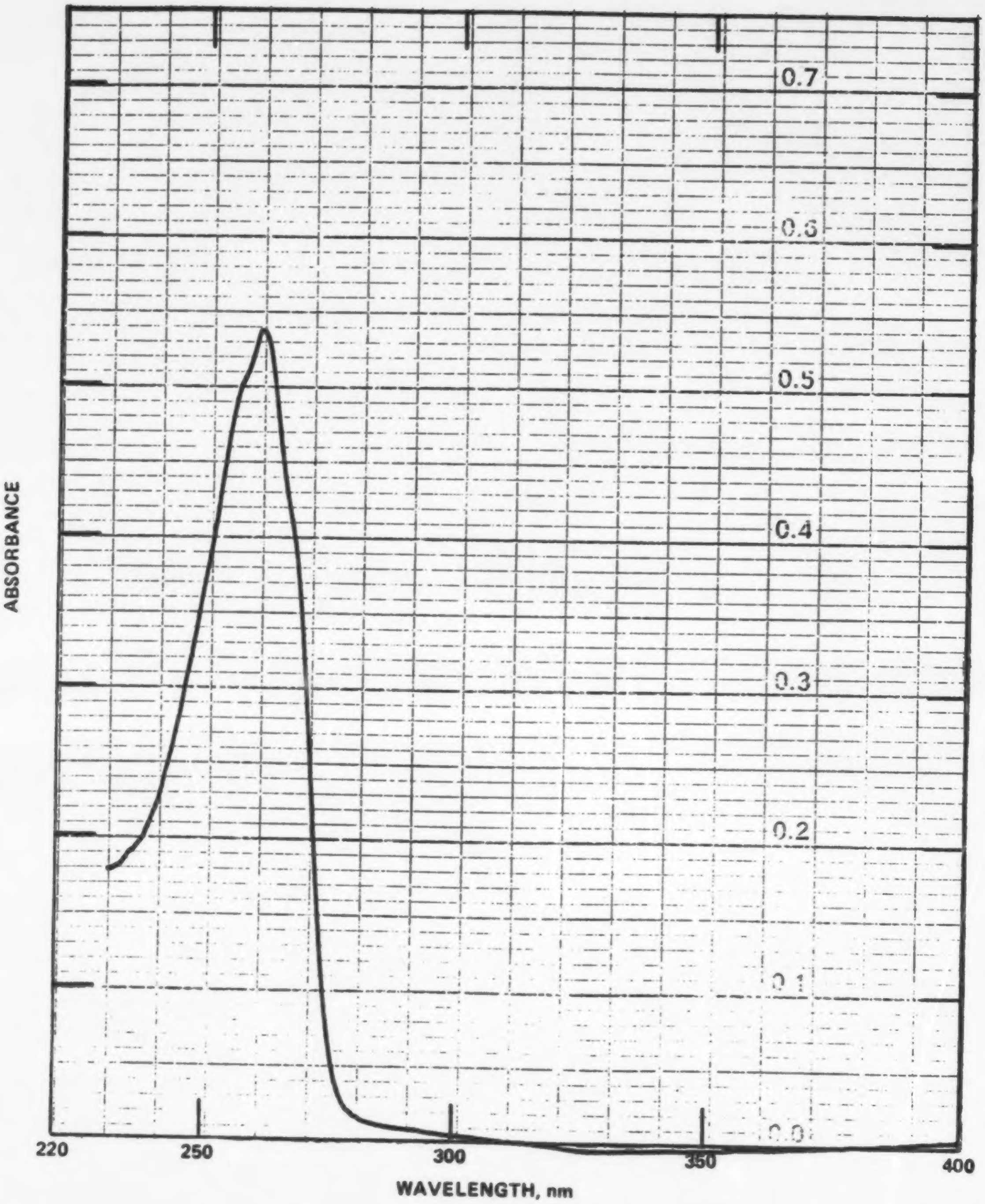

Figure C-125. UV spectrum for nicotine.

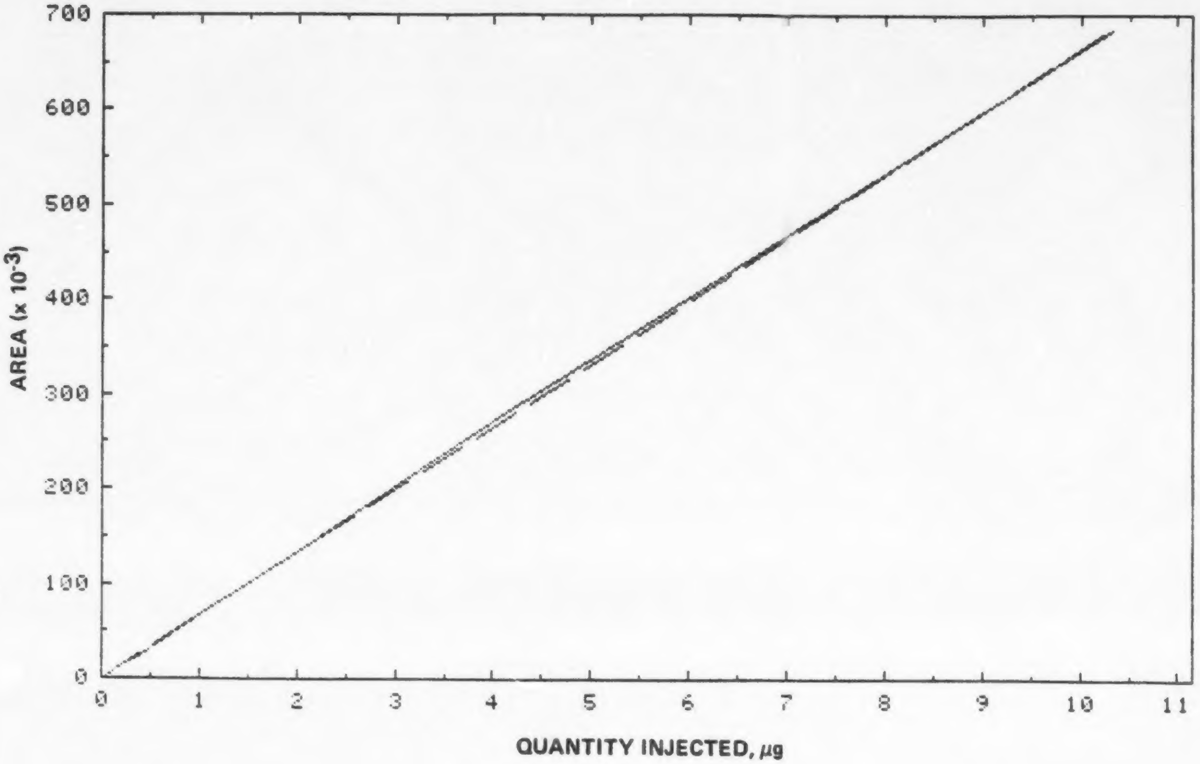

Figure C-126. Calibration curve for the determination of nicotine by HPLC/UV (254 nm).

Range: 0.041 - 10 µg
Correlation coefficient: 0.999
Slope: 6.66×10^{1}
y-Intercept: 1.07×10^{-1}

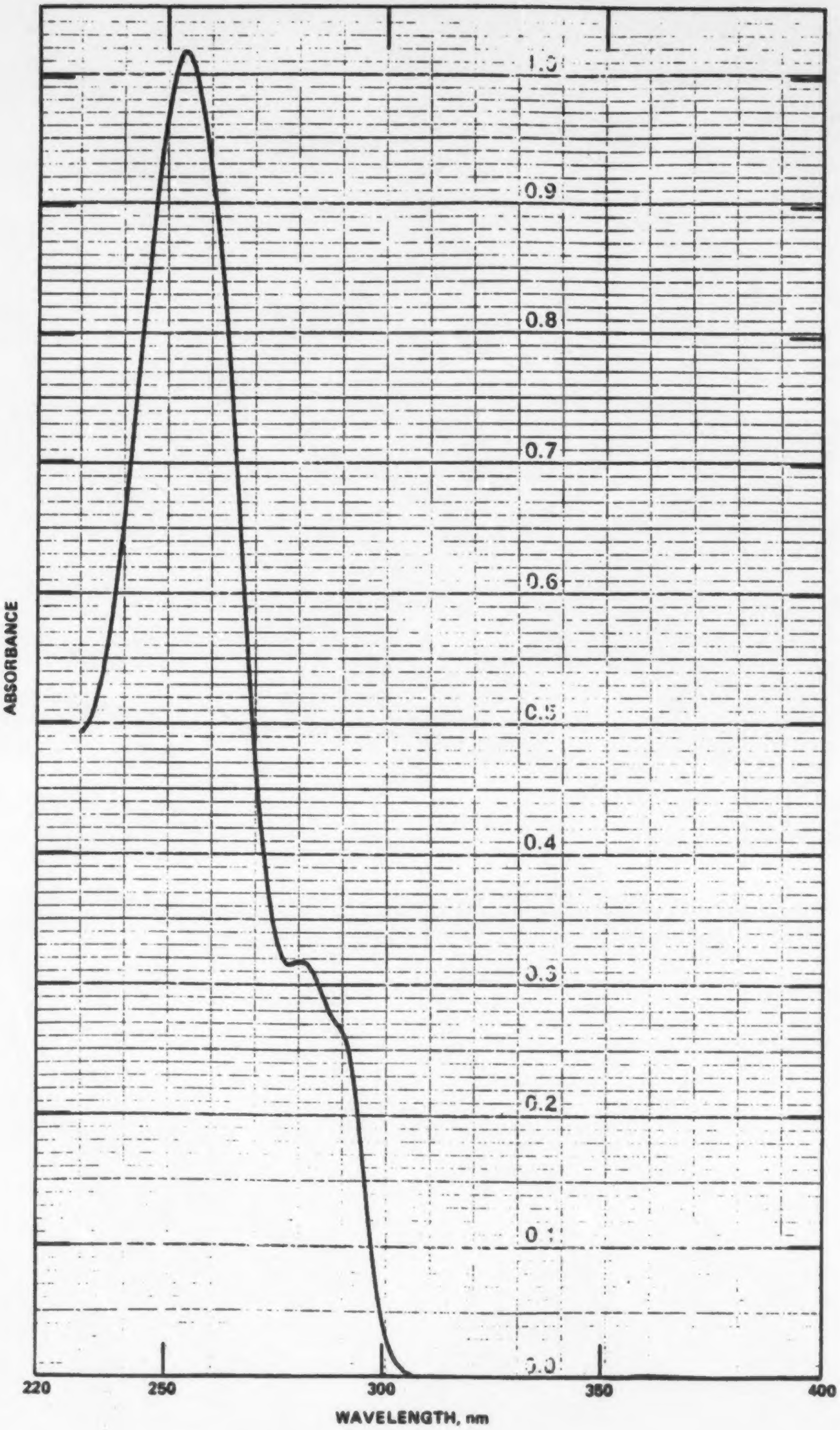

Figure C-127. UV spectrum for strychnine.

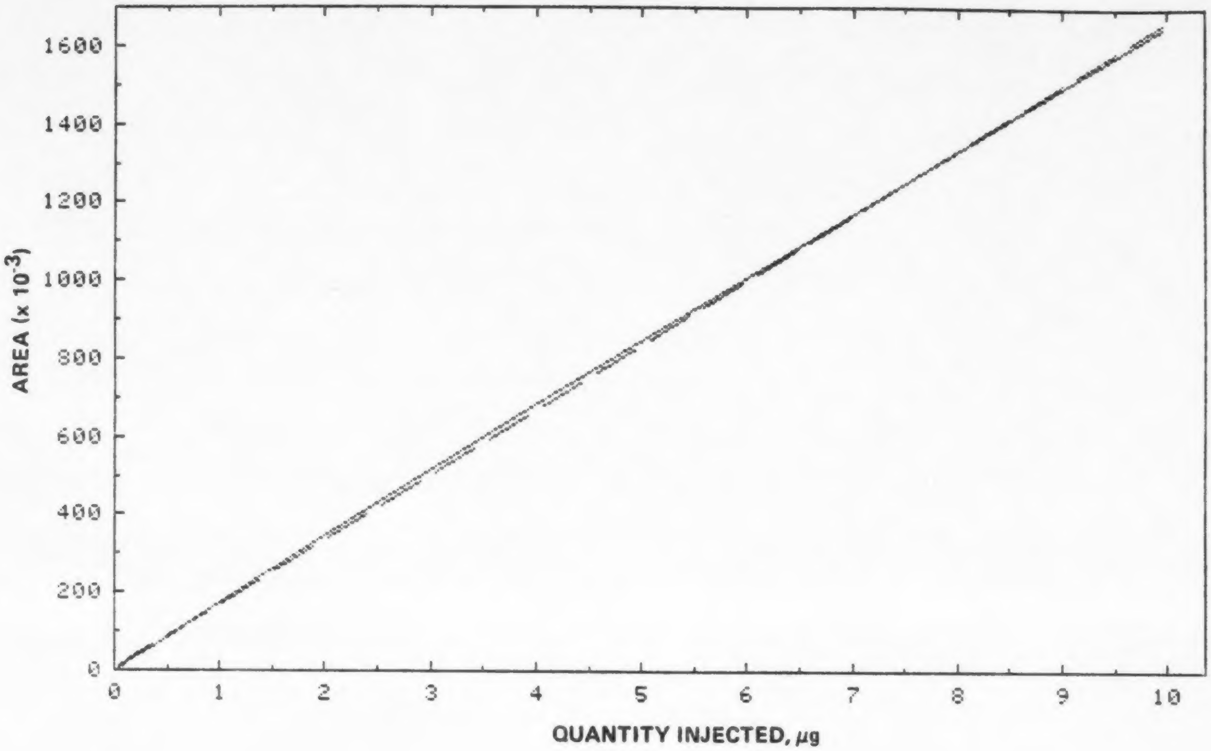

Figure C-128. Calibration curve for the determination of strychnine by HPLC/UV (254 nm).

Range: 0.10 - 10 μg
Correlation coefficient· 0.999
Slope: 1.66×10^2
y-Intercept: 4.39

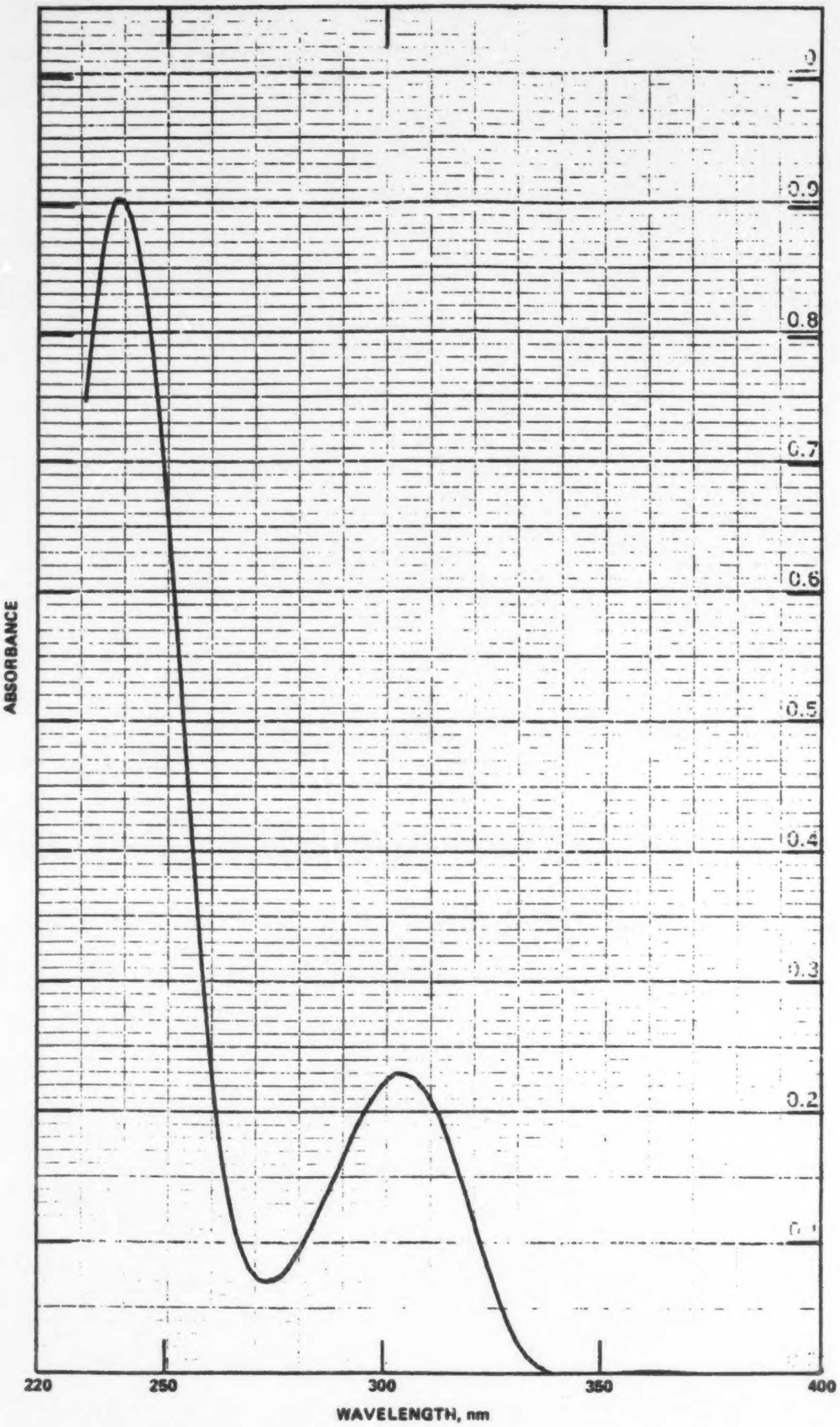

Figure C-129. UV spectrum for methapyrilene.

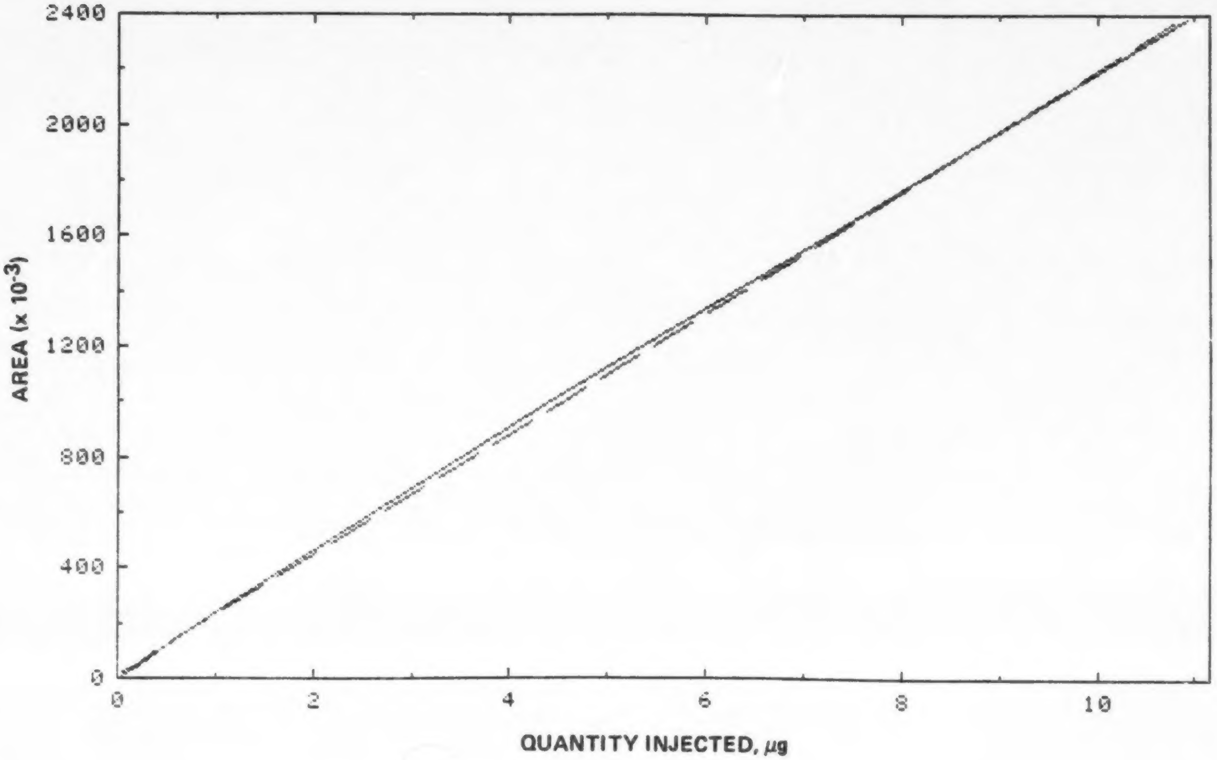

Figure C-130. Calibration curve for the determination of methapyrilene by HPLC/UV (254 nm).

Range: 0.22 - 11 μg
Correlation coefficient: 0.999
Slope: 2.18×10^2
y-Intercept: 1.13×10^1

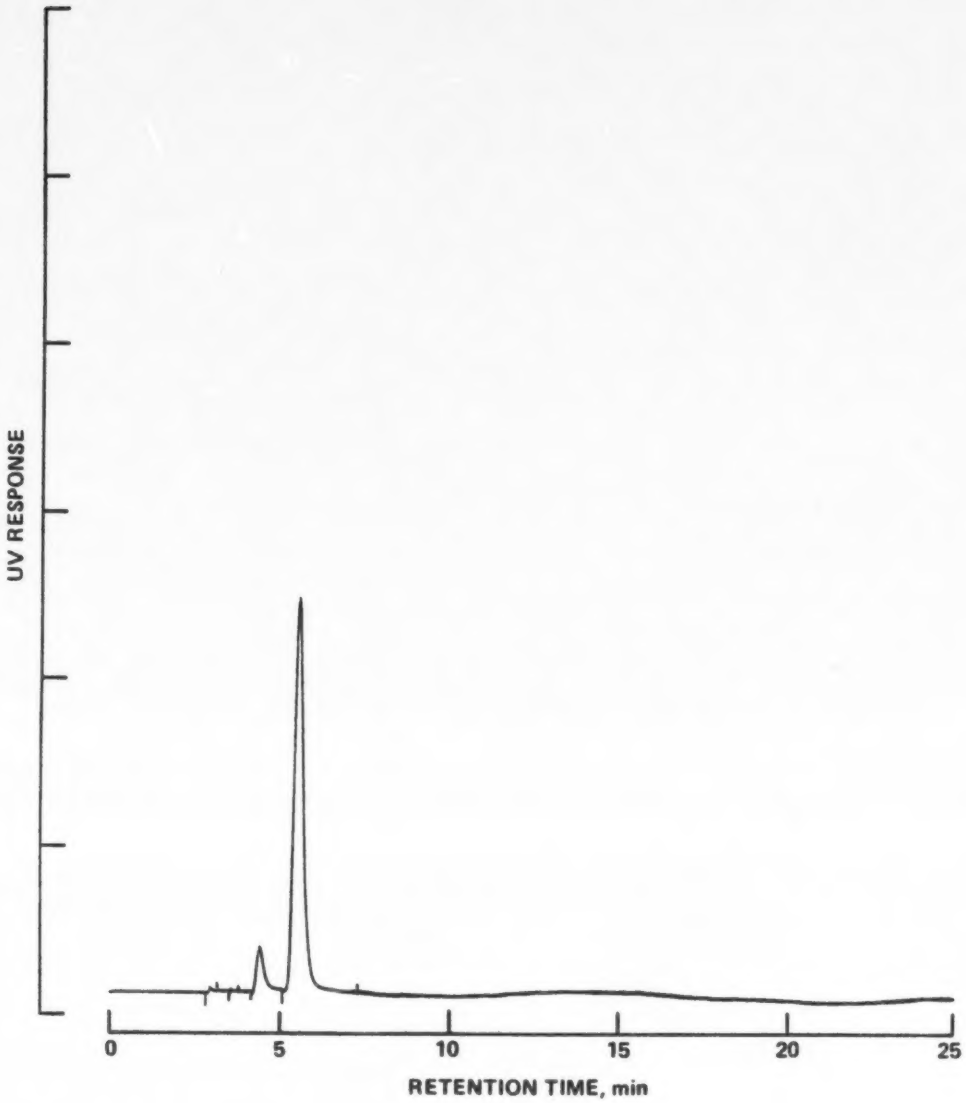

Figure C-131. Chromatogram by HPLC/UV (254 nm) for mitomycin C.

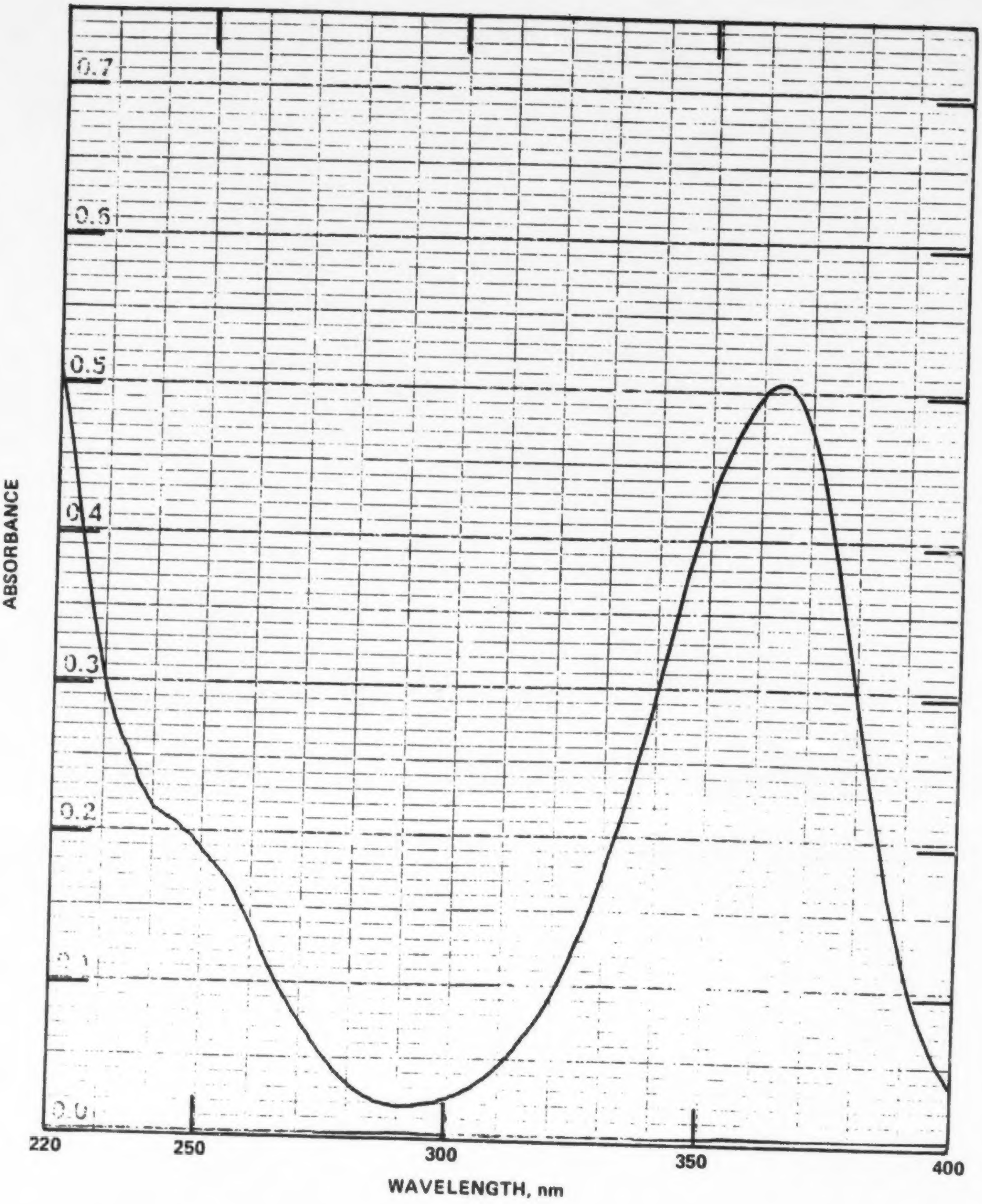

Figure C-132. UV spectrum for mitomycin C.

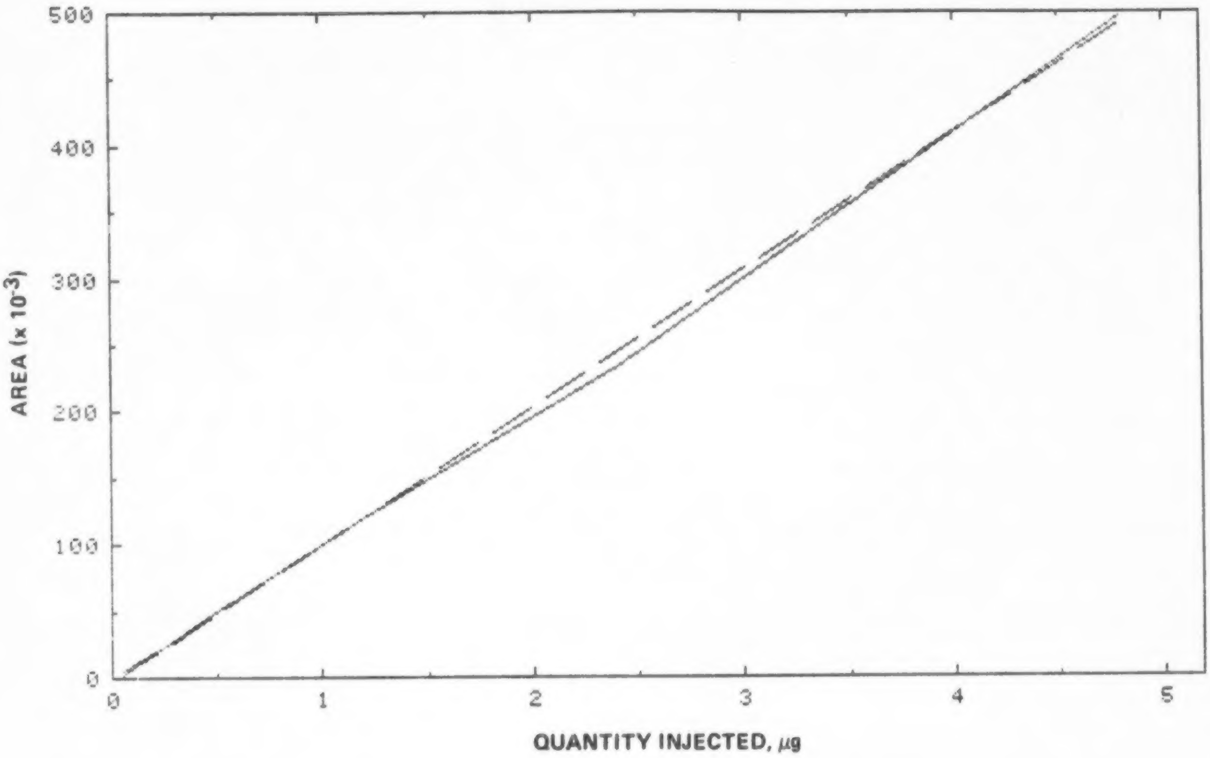

Figure C-133. Calibration curve for the determination of mitomycin C by HPLC/UV (254 nm).

Range: 0.12 - 4.8 µg
Correlation coefficient: 0.999
Slope: 1.03×10^2
y-Intercept: -2.70